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Physisorption of adenine DNA nucleosides on zigzag and armchair single-walled carbon nanotubes: A first-principles study

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Using first-principles calculations, we report the adsorption of adenine dinucleoside on single-walled carbon nanotubes (CNTs) with various diameters and chiral angles. The calculations indicate that in addition to noncovalent π-π interactions between the adenine base of dinucleoside and CNT, hydrogen bond interactions also develop between the sugar residue and the π orbital of CNT. The adsorption energy for the dinucleoside is between 1.50 and 3.80 eV for different CNTs. It exhibits a pronounced and specific dependence on the CNT band gap and diameter. For semiconducting zigzag CNTs, the adsorption energy decreases with increasing band gap. For armchair CNTs the adsorption energy increases with increasing diameter.

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I. INTRODUCTION

The interaction of biomolecules with single-walled carbon nanotubes (SWNTs) has generated a great deal of interest in the past few years.[1–3] Especially, the noncovalent interaction of DNA with carbon nanotubes (CNTs) (Refs. 4–6) attracts much attention. A large variety of potential applications in the nanodomain are at stake, from concerns about biological safety to fine tuning of electronic properties. One application which is of interest to the present study is the possible sorting of CNT based on selectivity in the DNA wrapping of CNTs as a function of diameter and band gap of semiconducting nanotubes. The selectivity of these methods can be further enhanced by vigorous centrifugation of prepared dispersions and the use of ion-exchange chromatography. The separation of metallic and semiconducting nanotubes is improved compared with other techniques, and separation on the basis of tube diameter has become possible. Understanding the mechanisms of the DNA-based separation approach is of both scientific and technological significance.[7–9]

Through selective adsorption CNTs may be suitable for electronic sensing of various odors. In this context the conducting properties of DNA and CNT are important.[10,11] The probing of conformational changes in DNA on SWNT also shows great potential for new detection mechanisms.[12] Meng *et al.*[13] developed an approach for determining the orientation of DNA base attached to carbon nanotube by combining *ab initio* time-dependent density-functional theory (DFT) and optical-spectroscopy measurements. This result sheds light onto the complex interactions in the DNA-CNT system, as a potential candidate for ultrafast DNA sequencing through electronic probes. Many papers[14–16] indicate that the interaction of DNA and CNTs is mediated by the π stacking of the aromatic bases of DNA to the graphenelike surface of CNT. Johnson *et al.*[6] reported a molecular-dynamic study about the self-assembly of the DNA-CNT nanosystem. The study reveals that CNT induce single-stranded DNA (ss-DNA) to undergo a spontaneous conformational change that enables it to adsorb on the CNT surface via the π-π stacking interaction of the nucleobases. Gowtham *et al.*[16] compared the physisorption of the different base molecules on a small-diameter (5,0) SWNT by first-principles methods.

So far these studies did not take into account the remarkable property of CNTs that they are either metallic or semiconducting, depending on the diameter and helical arrangement. A simple π-only tight-binding model predicts that the (n,m) nanotube is "metallic" when n-m is a multiple of 3, otherwise it is semiconducting.[17] This "1/3 rule" can be understood by starting with the graphene band structure and imposing the appropriate boundary conditions.[18] More detailed studies have shown that most metallic tubes are not gapless, except armchair tubes ($n=m$). When n-m is divisible by 3 but nonzero, the nanotube is a narrow-gap semiconductor because of hybridization between σ and π orbitals.[19] The effect is caused by the curvature of the tube; therefore it is very interesting to study the effect of the diameter of CNT on the adsorption mechanism and electronic structure of the combined system. Our aim is to obtain a better understanding of the bonding mechanism of DNA base with CNTs that differ both in diameter and chirality. In this present study, we have considered nine types of SWNTs—five zigzag ones and four armchair tubes—which cover an appropriate diameter range and highlight the difference between semiconducting and metallic tubes. We will specifically focus on the subtle difference in the adsorption strength of the DNA base on these different CNTs.

II. COMPUTATIONAL METHODS

The SWNTs which we examined are five zigzag tubes: (7,0), (8,0), (9,0), (10,0), and (17,0), and four armchair tubes: (4,4), (5,5), (6,6), and (7,7). We apply periodic boundary calculations using, for armchair SWNTs, a super cell consisting of eight unit cells, with a total length of about 19.01 Å along the tube axis. For zigzag SWNTs, the unit cell of length 3.94 Å was repeated five times along the tube axis. A lateral separation of 40 Å between tube centers was adopted, which was large enough to eliminate the interaction between the neighboring tubes. These dimensions were doubled for the calculation of the density of states (DOS) profiles for the isolated CNT. Helix formation for adsorbed oligonucleotides is found to be derived from electrostatic and torsional interactions within the sugar-phosphate backbone. In order to mimic the adsorption of the chiral ssDNA backbone, at least two adenine-sugar-phosphate units have to be used.[6] The adsorbed adenine nucleosides are linked by a phosphate bridge and terminated with a hydrogen atom. The sugar ring was included in order to generate an electronic environment for the nucleic acid base that resembles more closely the situation in DNA rather than that of individual isolated bases. Adenine was chosen because this is a bicyclic π system with a strong binding tendency.

Johnson *et al.*[6] investigated the structural stability of a poly G-T dimer on CNT by molecular dynamics and found that this arrangement induces high stress within the ssDNA sugar residues and glycosidic bonds. The sugar residue axis is almost parallel to the tube axis. Our simulation of the DNA adsorption on CNT was initiated with the long molecular axis parallel to the tube axis and the base almost parallel to the surface of CNT, which corresponds to the result from molecular dynamics.[6] The initial distance between the DNA bases and the SWNT wall was about 7.5 Å. This large distance easily allows obtaining the conformational minima upon geometry optimization.

Our calculations are based on first-principles pseudopotentials within density-functional theory as implemented in SIESTA,[20,21] which employs a localized orbital basis in the representation of wave functions. We use soft norm-conserving pseudopotentials and Ceperley-Alder exchange-correlation energy within a local-density approximation (LDA). The Ceperley-Alder version of the LDA was used for the electron exchange and correlation,[22] and optimized Troullier-Martins[23] pseudopotentials were used for the atomic cores in this calculation, which is more suitable than the generalized gradient approximation (GGA) to study weakly interacting systems such as the π stacking. A linear combination of numerical atomic orbitals with double-ζ polarizations (DZPs) is used in the basis set to describe the valence electrons.[24,25] Real-space integration was performed on a regular grid corresponding to a plane-wave cutoff around 300 Ry, for which the structural relaxations and the electronic energies are fully converged. Previous studies have indicated that LDA performs well for CNT study.[25] Mulliken charges were used for the calculation of the charge transfer. The net transfer is obtained by summation over all the atoms of DNA.[25]

III. RESULTS AND DISCUSSION

A. Adsorption mode and energy of the DNA nucleotides on SWNTs

The preferred configurations for the combined systems are all similar to the extent that the stable geometries are all slipped tangential ones (the cytosine ring considerably deviates from C6 ring), which is almost similar to the adhesion of adenine on a planar layer [see Fig. 1(a)]. Previous calculations of benzene on CNT[26,27] indicate that "bridged" configurations with the benzene molecule over a C-C bond are more favorable, which is very different from the geometries of adenine adsorbing upon a planar graphene layer. On a graphene layer, the N and C atoms of adenine are found to occupy the hollow sites of the hexagonal ring. However, on a CNT, because of the curvature of the nanotube, the C and N atoms of the base do not necessarily reside over the center of a hexagonal C ring; instead they can shift position to maximize the van der Waals (vdW) attraction between the C and N atoms of the base and C atoms of the CNT. The nucleoside binds on SWNT through its base part located between 3.0 and 3.2 Å away from the CNT's wall, which is in very good agreement with the report of aromatic molecules on small-diameter CNTs calculated by first-principles methods.[28] The base unit shows a slight bending around the nanotube to maximize the stacking interaction. In accordance with previous calculation,[29] the sugar residue is found to be more flexible. There is evidence for a noncovalent interaction between the sugar residue and CNT. In our calculation, the distance of a H atom of the sugar residue and the CNT wall is about 3.8 Å, which indicates that a weak hydrogen bond was formed between a H atom of the sugar residue and the π orbital of SWNT.

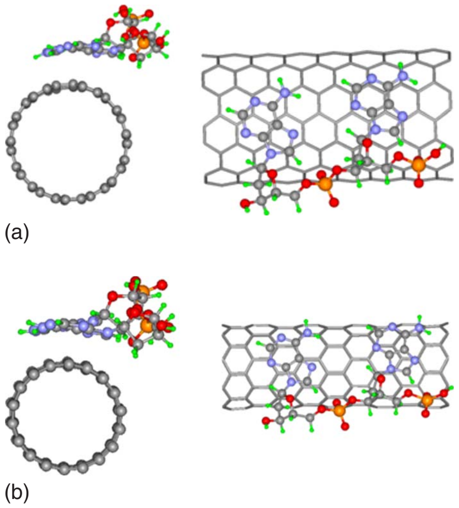

FIG. 1. (Color online) Equilibrium geometries of DNA on A (7,7) and B (9,0) CNT (left: top view; right: side view).

The adsorption energy of the DNA-CNT system was calculated using the following equation:

$$E_B = E(\mathrm{DNA/CNT}) - E(\mathrm{DNA}) - E(\mathrm{CNT}),$$

where $E(\mathrm{CNT})$ is the total energy for the isolated pristine tube, $E(\mathrm{DNA})$ is the total energy of the isolated DNA molecule, and $E(\mathrm{DNA/CNT})$ refers to DNA adsorbed on the CNT.[25] One must take into account that this procedure slightly overestimates the adsorption energy in view of the basis-set superposition error. The calculated energies are shown in Fig. 2. A general feature of our results is that the electronic properties of the CNT change when the DNA molecule is adsorbed and, moreover, that the adsorption energy is very much depending on the type of CNT and their diameters. Two factors were reported to affect the adsorption energies. One was the effective contact area between the adsorbed molecule and the sidewall of the tube and the other is the atomic correlation between the adsorbed molecule and

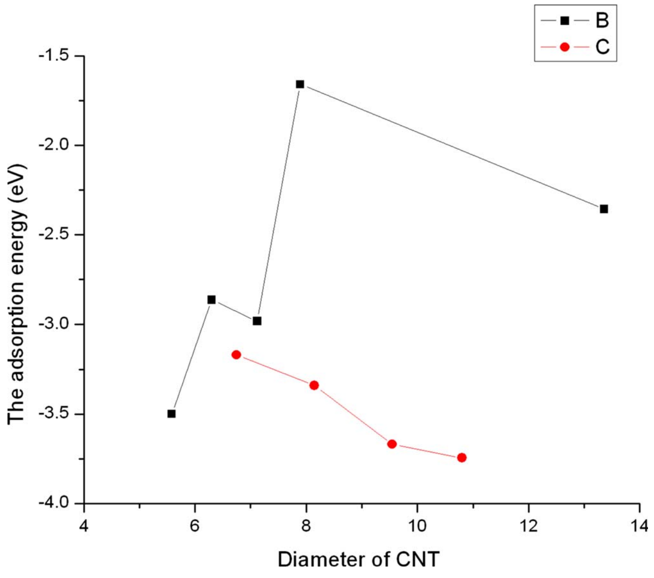

FIG. 2. (Color online) Calculated adsorption energies of DNA on different CNTs. [A: zigzag (7,0), (8,0), (9,0), (10,0), and (17,0); B: armchair (4,4),(5,5), (6,6), and (7,7)] (diameter in Å).

the sidewall of the tube. Lu *et al.*[28] reported that the π-π stacking interaction between nearly neutral aromatic molecules and SWNTs becomes dependent on the effective contact area and the atomic correlation. From Fig. 1, the base unit is seen to be bent around the CNT, which increases the contact area and atomic correlation. These are helpful to increase the noncovalent interaction between CNT and DNA.

The adsorption energies of the DNA molecule have been calculated for our collection of five zigzag and four armchair SWNTs. For the zigzag CNTs, the adsorption becomes less stable with the increase in the CNTs diameter except for the (9,0) and (17,0) CNTs. A similar trend was observed in quantum chemical calculations of the adsorption of cytosine upon fragments of $C_{24}H_{12}$, simulating several CNTs.[27] The reason for the exception is that the (9,0) CNT is metallic and can easily donate an electron as compared to the (7,0), (8,0), and (10,0) CNTs which are all semiconducting. In order to explain the observed trends we have calculated the band gaps for (7,0), (8,0), (10,0), and (17, 0); they are 0.16, 0.26, 0.48, and 0.27eV, respectively, in perfect correlation with the trends for the adsorption energy. This trend is also in line with published results, based on large cutoff plane-wave DFT calculations.[30] For the armchair SWNTs, the adsorption energy is stabilized with increasing diameter. This trend is compatible with the reported adsorption of benzene in a bridging position on CNTs reported by Tournus and Charlier.[26] From Fig. 2, there is an apparent selection of adenine toward metallic tubes versus semiconducting ones.

The calculated adsorption energy for DNA on nine CNTs ranges between 1.50 and 3.80 eV, which is almost twice the adsorption energy of adenine on graphite extracted from thermal adsorption spectroscopy. In fact, in our dimeric system, the DNA was composed of two adenines, which have four aromatic rings. Hence, in this combined system the adsorption energy mainly reflects the contributions of the four aromatic groups. Nonetheless the contribution of H-π interactions, between an H atom of DNA and the π orbital of SWNT, is not negligible. Lu *et al.*[1] reported that the hydrogen-bond distance between NH_2CH_3 and the CNT wall is about 3 Å and the interaction energy is about 0.18eV. The key role in the attraction energy is played by the polarizability of the adsorbed molecule. The polarizability of the base molecule, which represents the deformability of the electronic charge distribution, is known to arise from the regions associated with the aromatic ring, lone pairs of nitrogen and oxygen atoms. In the nucleobase, unlike in benzene, both factors are combined due to the presence of heterocyclic six- and five-membered rings, with also additional side groups containing NH_2, CH, O, and two strong electron-withdrawing phosphatide groups. This is an expected behavior for a system that draws its stabilization from van der Waals dispersion forces since the vdW energy is proportional to the polarizability of the interacting entities. The result is a strong noncovalent interaction between DNA and CNT. Zhang *et al.*[25] reported that the adsorption energy of the coenzyme flavin adenine dinucleotide (FAD) on CNT is −2.21 eV. Our results are very different from benzene adsorption on CNTs, where our calculations based on the SIESTA program confirm a very minute adsorption energy and electron transfer for benzene on (8,0) CNT.

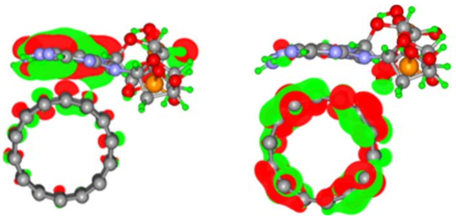

FIG. 3. (Color online) Molecular orbital of combined system for (7,0) CNT (left: HOMO; right: LUMO).

B. Charge transfer from carbon nanotube to DNA

In order to understand the interaction of DNA and CNT in detail, we have performed an analysis of the charge transfer between DNA and the SWNTs. The relevant frontier orbitals for the combined system are depicted in Fig. 3. The highest occupied molecular orbital (HOMO) is strongly hybridized between CNT and DNA. In contrast the lowest unoccupied molecular orbital (LUMO) is more localized on CNT. This indicates a strong π-π stacking interaction between CNT and DNA, where the aromatic molecules act as acceptor and the CNT as donor. The hybridization is stronger when the acceptor aromatic molecules are adsorbed on the wall of metallic SWNTs.

The calculated charge transfers between our set of CNTs and the nucleobases are plotted in Fig. 4. Some studies report that the transfer charge between aromatic molecules and CNT is very small and the resulting contribution to the adsorption energy from the attractive Coulomb interaction can be estimated to be at or below 0.01 eV.[31,32] However, for our combined system, the transfer charges from CNT to DNA are found to be larger than 0.4e. These findings are in line with the adsorption of 2,3-dichloro-5-dicyano-1,4-benzoquinone

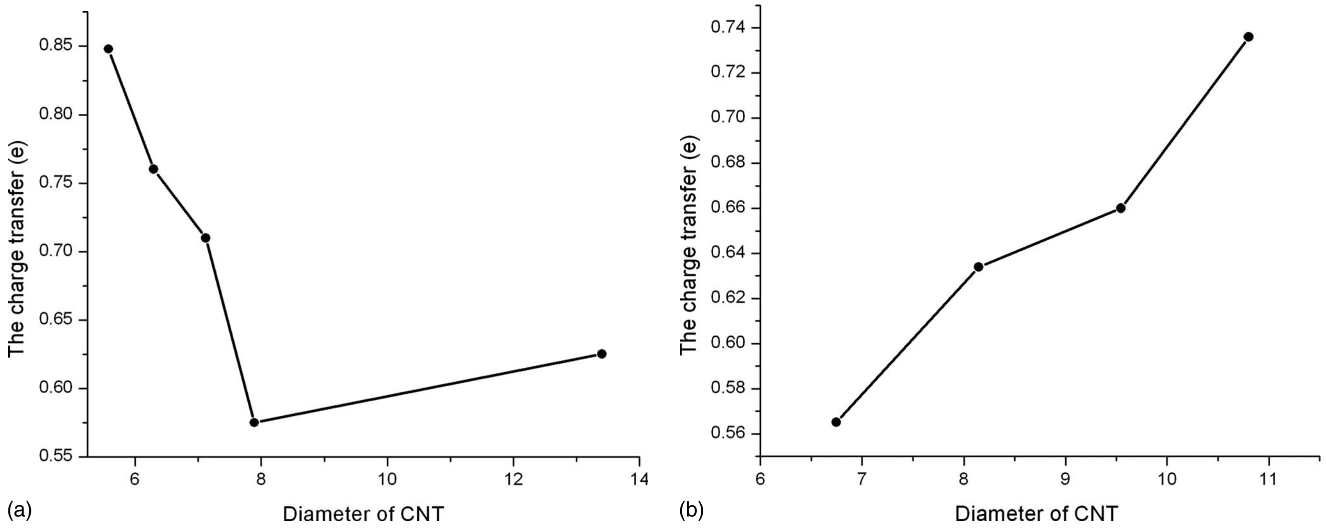

FIG. 4. Plots of the charge transfer to DNA from different diameter CNT. [(a) zigzag (7,0), (8,0), (9,0), (10,0), and (17,0); (b) armchair (4,4), (5,5), (6,6), and (7,7)] (diameter in Å).

(DDQ) on CNT which also involves a large transfer charge of 0.59*e* from DDQ to CNT.[28] The reason for a large charge transfer is threefold. First the DNA is known to be an electron acceptor, so it is expected that the charge transfer from CNT to DNA is larger than to other aromatic molecules and even more so for a dimer system. Second, because there are also several hydrogen bonds between DNA and the CNT π orbital, this will promote electron transfer. A hydrogen bond on the CNT surface can lead to charge transfer of about 0.1*e*.[1] Finally there are two strong electron-withdrawing phosphatide groups on DNA, which is another important reason for large charge transfer from CNT to DNA.

From Fig. 4(a), it is observed that the charge transfer will follow the same trends as observed for the adsorption energies. For the (7,0) SWNT, which has a diameter of 5.4 Å, the charge transfer is about 0.85*e*, and it gradually reduces to only 0.56*e* for the (10,0) tube. For the (17,0) large-diameter tube, which has a small band gap and larger adsorption energy, the charge transfer increases again slightly. For the armchair CNTs, the trend is exactly opposite; the transferred charge is about 0.56*e* for the smallest (4,4) tube and increases to 0.74*e* for the (7,7) armchair. Why is this charge transfer so large, and why so much dependent on the type of nanotube? For a detailed answer to these questions, we must consider the band gap of CNT and the density of states.

For semiconducting CNTs, the study of adsorption of fluorine molecules on CNT by Choi *et al.*[33] indicates that the adsorption energy is found to depend on the band gap. It is easy to understand that a small band gap will lead to large charge transfer from CNT to DNA fragment. For the isolated SWNTs the band gap for the (7,0), (8,0), (10,0), and (17,0) is 0.16, 0.26, 0.48, and 0.27 eV in our calculation, respectively. Thus, the charge transfer and adsorption energy will decrease with increasing band gap of CNTs. However, for the metallic CNTs, the band gaps are all very small (almost zero). In this case the strength of adsorption will mainly depend on the effective contact area between the adsorbed molecule and the sidewall of the tube. For armchair CNT, we expect that the adsorption energy will be largely influenced by the curvature effect that depends only on the diameter. So for armchair CNTs, the adsorption energy and charge transfer will increase with increasing CNT diameter. Based on the famous 1/3 rule the (n,m) nanotube is metallic when n-m is a multiple of 3, otherwise it is semiconducting. So, for the CNTs used in this study, all armchair and the (9,0) zigzag are metallic, but the (7,0), (8,0), (10,0), and (17,0) are semiconducting. The previous experimental and theoretical studies indicate that aromatic molecules exhibit stronger charge-transfer interactions toward metallic CNTs than toward semiconducting ones.[28,34] So, adsorption to the metallic (9,0) is indeed found to be stronger than for the semiconducting (8,0) CNT.

For further confirmation, we investigated the DOS of CNT/DNA. The DOS of the isolated CNTs was simulated with a larger unit cell to obtain a more accurate description. Figure 5 gives the DOS of DNA doped on (10,0).

It is obvious that the adsorption of DNA will lead to a reduction in the band gap from 0.48 eV to zero, and the

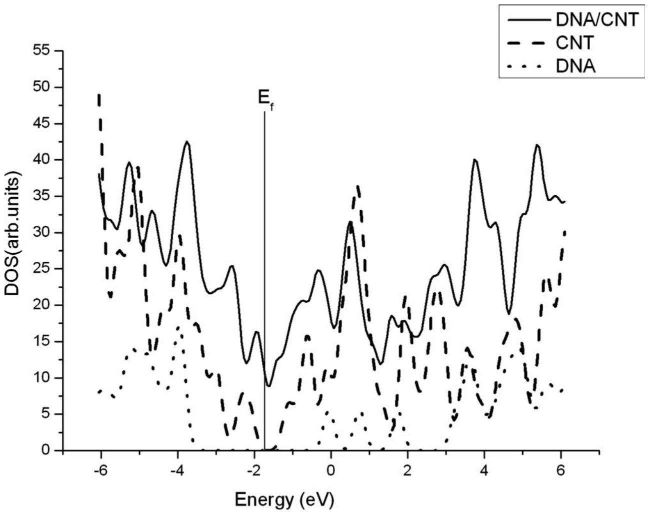

FIG. 5. Total density of states of combined system for (10,0) CNT.

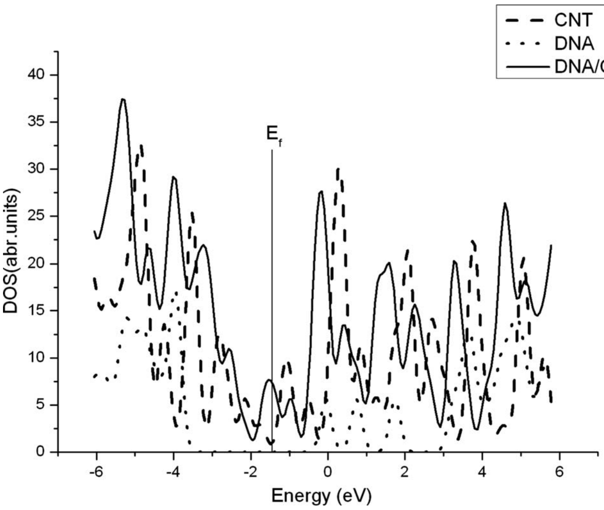

FIG. 6. Total density of states of combined system for (9,0) CNT.

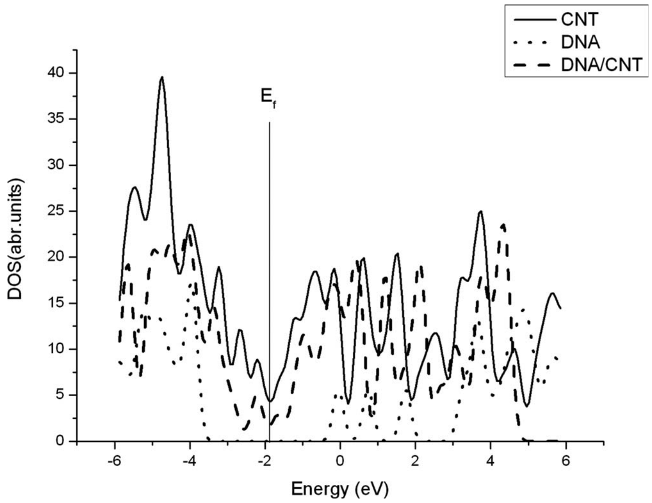

FIG. 7. Total density of states of combined system for (4,4) CNT.

combined system changes from semiconductor to metal based on the LUMO of DNA. Figures 6 and 7 give the effect of physisorption on the DOS for the metallic (9,0) and (4,4) CNTs, respectively. In comparison to the semiconducting tube in Fig. 5, it is clear that the contribution of the metallic CNT to the DOS of the combined system is more dominant. We also observe that DNA gives a significant contribution to the DOS of the combined system. This supports that there is a strong π-π interaction between DNA and CNT which is ascribed to the fact that π-π stacking gives rise to strong orbital hybridization between CNT and DNA, as was already evident from Fig. 2. All these results are very different from the adsorption of benzene on CNT because of the weaker π interactions of homoaromatic molecules. Hence one needs strong electron acceptors, such as DDQ, FAD, and DNA, which exhibit strong orbital hybridization to attain large adsorption energies.

IV. CONCLUSION

In conclusion, the adsorption of a DNA fragment on various CNTs has been studied with *ab initio* calculations using the density-functional theory approach. The calculations indicate that there does exist not only a noncovalent π-π interaction between the nucleobase and CNT but also a hydrogen bond between the H atom of DNA and the π orbital of CNT. The adsorption energy varies from 1 to 3.80 eV for different CNTs, which reflects strong π-π and hydrogen-bond interactions. We found that the adsorption energy strongly depends on the type of CNT and its diameter. The two main factors which influence the adsorption are the band gap and the curvature of the SWNT. For semiconducting zigzag tubes the adsorption energy correlates very well with the band gap. For the tubes with small diameter this actually implies that the physisorption decreases with increasing diameter. For the metallic armchair tubes the adsorption energy decreases with increasing diameter, reflecting the influence of decreasing curvature. The adsorption of DNA will reduce the band gap from semiconducting tubes. If the adsorption extends over the whole tube, the combined system is expected to become metallic. It is also verified that metallic SWNTs have a larger contribution to the DOS of the combined system than semiconducting CNTs. The DOS profiles confirm the molecular-frontier-orbital picture of strong hybridization between CNT and DNA as a result of π-π stacking.

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