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Adsorption of Cytosineon Single-walled Carbon Nanotubes

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Abstract

The adsorption of cytosine on metallic pristine single walled carbon nanotubes (SWNT) surface is investigated using density functional theory with local density approximation. On the SWNT, cytosine is physis orbed by taking the π-π interaction. Binding energy reported in this case is around -0.38 eV. By introducing metal atoms to the cytosine- SWNT, interaction can be strongly enhanced. The enhanced binding energies increases to -0.56 and -2.20 eV in presence of Li and Co atoms. Using pristine SWNT, electric sensor based on Co- doped SWNT depicts more sensitivity. Reported work gives insight into SWNT-based bio- sensors enhanced by doping appropriate metal atoms.

Keywords: SWNT; Cytosine; Adsorption; Biosensor

Introduction

After the successful synthesis of experiment [1], carbon nanotubes have attracted much more interest to the research community. Carbon nanotubes have potentials applications in various fields such as architecture, field-emission, molecular electronics, catalysis and bio-sensors [2-10].

The behavior of ds DNA molecule have been attached to SWCNT was investigated using molecular dynamics simulations [11], which reveals the π –staking interaction between nucleo bases and side wall of the nanotubes. The selectivity of single nucleo bases towards adsorption chiral single-wall carbon nanotubes (SWCNTs) using DFT [12], suggested adsorption energies of the nucleo bases has in the order of G>A>T>C which validates experimental work.

To improve the sensitivity of graphene doped by Al shows significant interaction with CO molecule [13], it attributes metal doping could enhance sensitivity of graphene.

The biomolecules such as DNA nucleo bases, adsorbed on carbon nanotubes and graphene surface are extensively studied by different research groups across the globe.

Theoretical Investigations reported in [14] shows that all nucleic acid bases (NABs) guanine, adenine, cytosine, thymine and uracil forms stable stacking with zigzag (7,0) single- walled carbon nanotubes. The interaction energy suggested that among the bases Guanine forms most stable stacking complex.

The interaction energy of nucleic acid bases with graphene and SWNT [15] using DFT-D and MP2 studied in terms of semiempirical molecular orbital method PM3 with dispersive corrections (PM3-D). These results predicates semiempirical approach is more accurate and cost effective. The binding energy of various nucleo bases Guanine, adenine, thymine and cytosine with (5, 5) SWNT [16] reported by applying the first principal HF method.

The binding energy, physisorption, understanding of binding mechanism, interaction of nucleo bases phenomena with carbon nanotubes (SWNT) i.e. conducting, semiconducting have been investigated theoretically and experimentally respectively [17-39].

To exploit the potential of the applying single walled carbon nanotubes (SWNT-6,6) as sensing material, it is very important to understand an interaction between the SWNT(6,6) surface and adsorptive molecules. It is known that such types of interaction are dominated by chemical natures of the molecules and particularly preferential adsorption sites. Most of previous published investigations focused on interactions or adsorption of bimolecular (DNA) onto pristine single walled carbon nanotubes. To understand the effects of adsorption/doping of the bimolecular-SWNT interaction is still very limited. In this work, we investigated the adsorption of cytosine on pristine single walled carbon nanotubes (SWNT-6,6) and metal-doped SWNT(6,6), applying first-principles calculation.

Computational Methods

The calculations were performed in the framework of density functional theory with a plane wave basis set. To obtain stable atomic geometries and binding energies we used the Vienna Ab initio simulation package (VASP) [27] with ultra-soft pseudo potentials [28]. This approach makes carrying out numerous computations feasible for system with a large number of atoms per unit cell. We expanded the cutoff energy was increased up to 29.1 Ry (396 eV) to cheek the convergence of the result, further, we calculated exchange-correlation potential within the generalized gradient approximation (GGA) [29].

Each system consists of a 12.30 × 12.30 × 10 Å SWNT super cell (96 C atoms) with cytosine molecules adsorbed. We used a 1 × 1 × 3 Monkhorst–Packgrid [30] fork-point sampling of the Brillouinzone. The *k*-point is set to 3 × 3 × 1 for the Brillouin zone integration. The structural configurations of the isolated SWNT (6, 6) are optimized through fully relaxing the atomic structures. With the same super cell and *k*-points sampling, the configurations of the different molecule-SWNT systems were optimized through fully relaxing the atomic structures until the remaining forces are smaller than 0.01 eV/Å. The binding energy of cytosine on SWNT is calculated as

$$E_{ad} = E_{(molecule@SWNT)} - E_{(SWNT)} - E_{(molecule)} \quad (1)$$

The above calculation method was tested on a well-known system, e.g. the interaction of (6, 6) SWNTs with benzene, and reported binding energy of -0.12 eV, which is consistent with the previous reports [31].

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The electron transport calculations were performed using the Atomistix Tool Kit (ATK) 2.0.4 package [32], which were implements DFT-based real-space, nonequilibrium Green's function (NEGF) formalism. The mesh cutoff is chosen as 200 Ry to achieve a reasonable balance between calculation efficiency and accuracy.

Results and Discussion

To know nature of the cytosine and SWNT (6, 6) the chemical, simulated structures have been shown in (Figures 1a-1d) respectively.

To find the most favorable adsorption configurations, the molecule under investigation was initially placed at different positions above the graphene with different orientations. Figure 2 shows the possible adsorption configurations of cytosine on pristine and metal doped graphenes. For convenience, the adsorption configurations shown in Figures 2a-2e are referred as hollow, bridge and stack configurations, respectively.

The corresponding binding energy for different configures are tabulated in Table 1. In Table 1 adsorption energy (E_{ad}), equilibrium SWNT-molecule distance (d) which is defined as shortest atom to atom distance, and Mullikan charge (Q) of cytosine absorbed on metallic SWNT (6, 6) the stack configuration has a higher binding energy (-0.38 eV) than the hollow (-0.16 eV) or bridge (-0.26 eV), hence is the favorable adsorption configuration. Only small charge transfer occurs in all the three configurations, which clearly shows that the interaction is physisorption. The mechanism of the interaction is attributed to π-π stacking. The calculated binding energies are close to that reported for the nucleoside/SWNT (-0.42 to -0.46 eV) [14] adenine/carbon nanotubes (-0.35 eV), [15] andinteraction energy of nucleic acid bases with graphene and carbon nanotubes [16] and Binding of nucleo bases with single-walled carbon nanotubes systems [17].

Two atoms were used to dope the metallic SWNT (6, 6). To study the effect of metal doping in the optimize structure of SWNT-Li-Cytosine; practically there is no deformation in the geometry of SWNT and cytosine. In short, both remains near planer. Two hydrogen of the cytosine tilt slightly towards the SWNT (6, 6) between Li atom and cytosine is 2.26 Å, (Figure 3a) the distance i.e. shortest atom to atom distance is 2.26 Å, But in case of the geometry of the cytosine becomes deformed after adsorbing onto the Co-doped SWNT (Figures 3b and 3c) shows strong interaction taking place. The distance between Co and cytosine is 1.95 Å. The reported binding energies are 0.56 and -0.20 eV for Li and Co doped single walled carbon nanotubes which confirms the Co doped SWNT's shows a stronger binding to bio molecule cytosine than Li doped SWNT's (6, 6). Figure 3 compares the electronic total charge density plot of the cytosine@Li-SWNT (6, 6) with that of the Co-SWNT (6, 6) the small gap of the electron orbital appears between Li atom and cytosine (Figure 3b). Whereas in case of the cytosine@Co-SWNT (6,6) the electronic charge strongly overlapped, which leading to more orbital mixing and a large charge transfer. The Mullikan

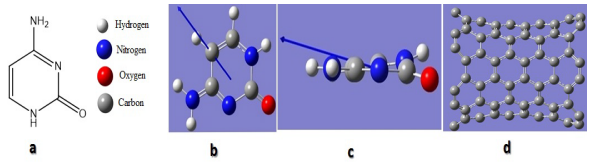

Figure 1: The schematic view of the cytosine: Chemical structure (a) ,simulated structure at 6-31+ + (b) C, N, O, and H atoms are shown as grey, blue, red and white respectively(b), top view cytosine (c) SWNT(6,6) (d).

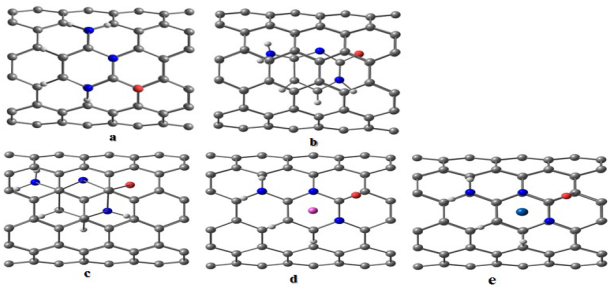

Figure 2: Schematic view of the cytosine adsorbed on SWNT (6, 6) with different configurations: (a) hollow (b) bridge (c) stack (d) Li-doped with SWNT and (e) Co-doped with SWNT.

System	E_{ad} (eV)	*d* (Å)	*Q* (e)
Cytosine@hollow SWNT(6,6)	-0.16	2.99	0.06
Cytosine@bridge SWNT(6,6)	-0.26	3.08	0.09
Cytosine@stack SWNT(6,6)	-0.38	2.91	0.04
Cytosine@Li SWNT(6,6)	-0.56	3.23	-0.42
Cytosine@Co SWNT(6,6)	-2.20	3.09	-0.61

Table 1: Adsorption energy (E_{ad}), equilibrium SWNT-molecule distance (d) (defined as the shortest atom-to-atom distance), and Mulliken charge (Q) of Cytosine adsorbed on SWNT (6, 6).

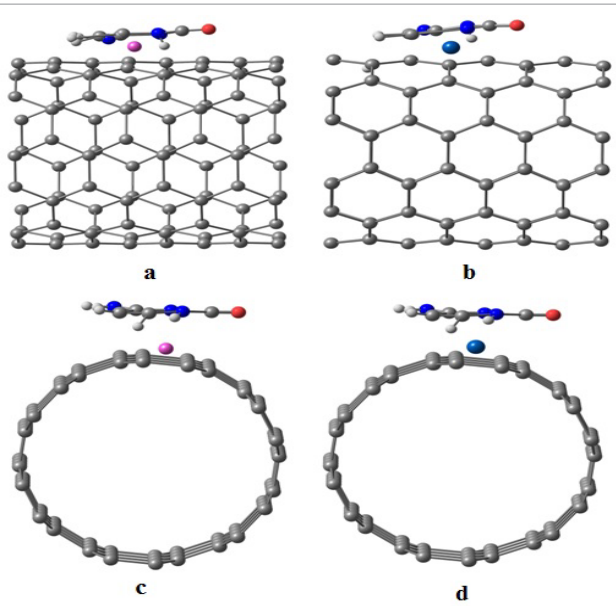

Figure 3: Schematic view of the cytosine adsorbed on SWNT (6, 6) with different configurations: (a) hollow (b) bridge (c) stack (d) Li-doped with SWNT& (e) Co-doped with SWNT.

population analysis reveals, the Co loaded on +1.92 were considered as positively charged ion in the adsorption adduct. The large charge (-0.61) is transformed from SWNT to cytosine in the presence of Co atom with high binding energy, depicts a strong chemical bond formed between the cytosine and Co-SWNT (6, 6) ,this reflects in the Table 1.

Figure 4 indicates the total electronic charge density of states (DOS) for the stack (Figure 2c) also metal doped configurations (Figures 2d and 2e) respectively. Comparing with the metallic single wall carbon nanotubes (6, 6), the DOS of cytosine SWNT system indicates very minute change near the Fermi level (Figures 4a and 4b), on adsorption

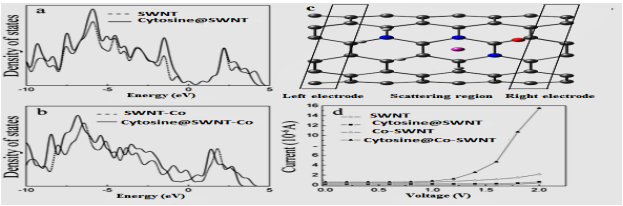

Figure 4: The DOS of (a) The pristine SWNT (dashed line), Cytosine-SWNT (solid line) (b) Co-SWNT (dashed line), Cytosine SWNT-Co (solid line) calculated for the corresponding configurations shown in Figure 4 (c,d). (c) A schematic illustration of the SWNT-based chemical sensor for detecting cytosine. (d) A comparison plot of the I-V curves for the devices based on SWNT, Cytosine@SWNT, Co-SWNT, cytosine@Co-SWNT.

there is no significant conductivity changes. The minute or little change in DOS near the Fermi level is consistent with relative to small binding energy. When the cytosine adsorbed on Co-doped SWNT a abrupt change occurs near the Fermi level which is agreement with the high binding energy values. Therefore we conclude that metallic SWNT cannot suitable for cytosine as sensing material, whereas Co-doped SWNT shows high sensitivity.

To study the sensing properties of the metallic single wall carbon nanotubes (6,6), the electron transport properties and Co-doped SWNT were simulated using NEGF methods. The chemical sensing transducer is the resistance sensor which is the simplest one. In this type resistance change of the sensing materials upon the adsorption of chemicals is detected. SWNT-based resistance sensors are simulated using a model consisting of SWNT(6,6) contacted by two SWNT electrodes as depicted in Figure 4c, we determined series of current versus voltage (I-V) curves for SWNT junction with and without the adsorption of cytosine. The simulated I-V curves for the metallic SWNT and Co-doped SWNT before and after cytosine adsorption are shown in Figure 4d.

The SWNT shows nonlinear behavior. The Co-SWNT is more conductive than the metallic SWNT (6,6) due to the possibility that the π states of the SWNT are hybridized with 4s and 3d levels of the Coin the DOS near the Fermi level [40]. The I-V curves shows that the Co-SWNT has the highest response to cytosine. When the bias voltage is higher than 1.5 V, the Co-SWNT shows a sensitivity one magnitude higher than that of the metallic single wall carbon nanotubes.

Conclusion

Investigated calculations suggested that the cytosine have a very weak interaction with pristine single walled carbon nanotubeSWNT(6-6) surface. Therefore, chemically or physically modify SWNT are required for more effective adsorption to this molecule. We investigated that strong binding can be achieved by introducing metal atoms on the SWNT surface. Particularly, the Co-doped SWNT shows strong interaction with cytosine and consequently exhibits much higher sensitivity than the pristine SWNT. Reported result provides useful to develop novel SWNT -based for immobilization as well as detection of DNA molecules on SWNT surface.

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