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DFT studies of functionalized carbon nanotubes as nanoadsorbent of a benzimidazole fungicide compound

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Abstract. Using density functional theory calculations, we investigated properties of a functionalized carbon nanotube with one mercarzole molecule as a benzimidazole fungicide. Three different configurations are possible depending on the type of functional group used in the structure of mercarzole. We investigated different electronic properties for these configurations such as adsorption energy, band gap energy and charge transfer effects. As a consequence of structural properties the adsorption height and the most stable adsorption configuration are also discussed. It has been found that a mercarzole molecule is adsorbed on the tube surface with adsorption energies in the range of -0.01 to -0.67 eV, and their relative magnitude order is found as follows: imin group > ester group > amin group. Obtained results reveal important features of the adsorption mechanism of mercarzole molecules onto the functionalized carbon nanotubes. This study can be used in farming researches in order to improving cultivation and wellbeing human.

Keywords: molecular graph, eccentricity, Mercarzole, Adsorption, DFT, functionalized carbon nanotube
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1 Introduction

Nanomaterials have attracted great interest in recent years because of their excellent mechanical, electrical, electronic, optical and magnetic properties [1]. Since the discovery of

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carbon nantotubes (CNT) [2], these important one-dimensional systems have received extensive attention as promising building blocks for future nanoelectronics, nanodevices and nanosensors because of their small size, high chemical and thermal stability, high elasticity, high tensile strength and extraordinary electronic properties [3, 4]. Notably, in spite of its attractive properties, the poor solubility have hampered the future application of CNT in sensing or adsorbing of materials in aqueous solutions. In this sense, one proposed strategy like chemical treatment of CNT in an oxidizing environment, in which the oxygen-containing groups such as -COOH, -COO and -OH are introduced to the ends and surface of the tubes [5].

Mercarzole (MCZ, methyl 2-benzimidazolecarbamate) is a benzimidazole fungicide widely used in farming for protecting from and eradicating a variety of pathogens which affect fruits and vegetables [6]. This compound, when applied on soils, can remain for a long time, because the benzimidazolic ring is difficult to break and consequently its degradation is slow [7]. Therefore, the ability to quickly and correctly determine trace amount of MCZ has become increasingly important for the environment and health protection. The methods most frequently used for measuring benzimidazole fungicides were high-performance liquid chromatography, mass spectroscopy, UV-vis, fluorescence spectroscopies and electrochemical techniques [8]. Due to the difficulty with experimental measurement for biological and environmental systems, theoretical calculations, particularly density functional theory (DFT), has been widely used to study and evaluate the interaction of materials.

Within this work, we carried out a DFT study on the interactions of a MCZ molecule, with the surface of a functionalized CNT with one carboxyl group (FCNT), consequently adsorbing energies, electronic properties in the adsorption process of a MCZ molecule on the FCNT were investigated. Obtained results from DFT calculations may be useful for further studies in sensing and adsorbing of this greatly used fungicide.

2 The model and method of calculation

The full geometry optimizations and property calculations were performed with the quan tum-ESPRESSO package [9]. The widely applied generalized gradient approximation (GGA) with the exchange-correlation functional parameterized by Perdew, Burke and Ernzerhof (PBE) and the double numerical plus polarization (DNP) basis set were used [10]. The Brillouin zone was extracted from $2 \times 2 \times 4$ Monkhorst-Pack k-points meshes, to ensure convergence [11]. All of the proposed models are calculated in the same periodic supercell, with the periodic boundary conditions (PBC) [12] and the same k-point sampling grid, used spin unrestricted calculations and solvation model with water solvent, to ensure agreement between calculations. The adsorption energy E_{ads} is defined as the following equation:

$$E_{ads} = E_{complex} - E_{MCZ} - E_{FCNT}. \tag{1}$$

Where E_{MCZ} and E_{TFCN} denote energies of the free MCZ molecule and the functionalized CNT, respectively, and $E_{complex}$ indicates the total energy after adsorption. Moreover, the

HOMO/LUMO gap (E_g) is resulted as the Eq. (2):

$$E_g = E_{LUMO} - E_{HOMO}. \tag{2}$$

E_{LUMO} and E_{HOMO} signify the energies of the Lower Unoccupied Molecular Orbital and Higher Occupied Molecular Orbital.

3 Results and discussion

The interaction mechanism between MCZ and FCNT was studied by DFT method. Notably, presented results in this work are based on a hexagonal supercell of zigzag (10-0) carbon nanotube (CNT). A $2 \times 2 \times 4$ supercell of (10-0) CNT containing 200 carbon atoms was full geometry optimized. The dimensions of applied supercell were a=35.00, b=35.00 and c=21.12 Å, with the vacuum spacing about 15 Å between the tubes in adjacent supercells. The length and diameter of optimized bare CNT were computed to be about 21.12 and 7.97 Å, respectively. Notably, the calculated diameter of CNT was comparable with its value in literature [13]. Then, based on experimental functionalization of CNTs, a single carboxyl functional group was attached to a carbon on the external surface of CNT. Then, the functionalized CNT (FCNT) was calculated in the same periodic supercell, with the same plane wave cutoff energy, the same k-point sampling grid and the same DFT approach to ensure consistency between calculations. The geometry of the optimized FCNT was shown in Fig. 1a. The value of Eads and the bond length of carbon atom in carboxyl group and carbon atom on the surface of CNT were -0.77 eV and 1.57 Å, respectively, which indicates that carboxyl group was bonded to the CNT. The interaction of functionalized (10-0) zigzag CNT with a single MCZ molecule was considered. To find adsorption behavior of MCZ on FCNT, one MCZ molecule was located near (about 2 Å) the carboxyl group above the surface of FCNT. The molecule was positioned above the surface of tube with different starting orientations. To study MCZ adsorption, the MCZ are positioned in a number of configurations at the surface and then a full relaxation is performed within a fixed supercell. Fig. 1b presents optimized MCZ molecule and three proposed models for different possible orientation of MCZ on the surface of FCNT. In Model A, the structure of interaction imin functional group with carboxyl group on tube was constructed. Models B and C were constructed by interaction of amin and ester groups of MCZ with carboxyl group on the surface of CNT, respectively. We proposed three configurations for the adsorption of MCZ on the FCNT. In configuration A, B and C, imin (and amin in the benzimidazole ring), amin (out of benzimidazole ring) and ester functional group interacted with FCNT, respectively, Fig. 1b.

The energy difference between the HOMO and LUMO orbitals, (HOMO LUMO gap, Eg) for the pristine, FCNT, A, B and C models were listed in Table 1. For models A, B and C, the adsorption energies were calculated to be -0.67, -0.01 and -0.28 eV, respectively. The negative adsorption energy signified that MCZ adsorption is stable. The geometry optimizations of A, B and C have been shown in Fig. 2. The calculated charges transferred from the MCZ molecule to the functionalized tube are listed in Table 1, too. According to Table. 1, the

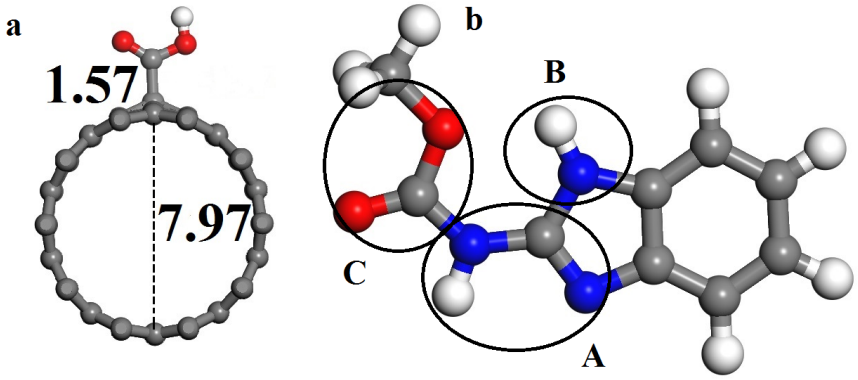

Figure 1. (a) Front view of (10-0) CNT optimized supercell; the distances are in angstrom. (b) The optimized MCZ with represented three different configurations A, B and C. gray, white, red and blue balls represent C, H, O and N atoms, respectively.

Table 1. Adsorption energy (Eads), HOMO-LUMO gap (Eg), charge transferred (Q) and adsorption bond length of MCZ on the surface of FCNT.

Model	$E_{ads}(eV)$	$E_g(eV)$	$Q(e)$	Adsaorption bond length (Å)
A	-0.67	0.12	0.48	1.08
B	-0.01	0.06	0.02	2.61
C	-0.23	0.6	0.03	1.68
FCNT	-0.77	0.06	0.00	
CNT		0.66		
MCZ		3.85		

analysis of the Mulliken atomic charges showed that the Mulliken charge transfer from N to carboxyl group is about 0.48 electrons for the configuration A. The relative adsorption energies of the MCZ on FCNT in the investigated configurations follow the order: A>C>B. The adsorption energy magnitude of the configuration A is significantly larger than that of the others. Also, the lowest distance and the most large charge transfer between MCZ and FCNT surface observed from configuration A. Obtained results indicate that the adsorption behavior of MCZ on the surface of FCNT is physisorption in three proposed configurations and FCNT could be considered as a suitable sensor for adsorption of MCZ in analysis.

4 Conclusions

The adsorption of one MCZ molecule on the exterior surface of a functionalized carbon nanotube (FCNT) has been investigated using density functional theory. It has been found that MCZ molecule is adsorbed on the tube surface with adsorption energies in the range of -0.01 to -0.67 eV. The most stable obtained configuration is that in which the MCZ molecule

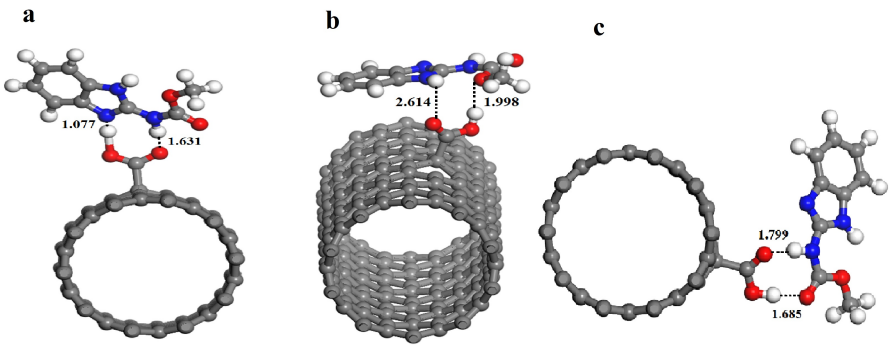

Figure 2. (a), (b) and (c) Optimized adsorption of the configurations A, B and C of MCZ on FCNT, respectively; bond lengths are in angstrom.

has been adsorbed above the carboxyl group of the FCNT tube surface via its imin group. The obtained results suggest that the FCNTs may be potentially used in MCZ adsorption that can be useful in detection of MCZ in farming studies. Theoretical calculations were performed to characterize the behavior of MCZ molecule adsorption on the external surface of functionalized (10-0) CNT with carboxyl group. Obtained results revealed the lowest adsorption energy for the configuration A. Moreover, due to the physisorption ability of FCNT toward MCZ, FCNTs can be considered as a suitable electrode modifier choice. The low and negative value of Eads and negligible effect on the electronic structure of FCNT indicates that FCNT is a suitable sensor for MCZ analysis.

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