

Organic pollutant adsorption on pristine, defected and Al-doped carbon nanotube: a dispersion corrected DFT study

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The effective enrichment and detection of organic pollutants in the environment has been attracted many attentions because of the enormous human health concerns. Using dispersion-corrected density functional theory (DFT-D2), we studied the interactions between 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) and pristine, defected and Al-doped carbon nanotubes. The TCDD molecule physical adsorption on pure and defected CNTs with a binding energy of about -0.52 eV and -0.34 eV. The accuracy of our method was validated by hybrid B3LYP levels of theory and it was shown that there is worthy agreement between two respected methods. However, the binding energy rises to -0.85 eV when TCDD binds to Al-CNT. The increase in binding is due to charge transfer from the TCDD molecule to the Al-CNT. Furthermore, the obtained DOS spectra show that the electronic properties of Al-CNT change considerably by the adsorption of TCDD whereas no such variations are observed for the other considered CNTs. Consequently, the Al-CNT is a promising candidate for the TCDD sensing and detection. Our *first-principles* results present evidence for a rational benchmark for the applicability of the Al-CNT for TCDD adsorption and detection.

Keywords: Al-doped CNT; TCDD; DFT-D; adsorption; Hazardous materials

INTRODUCTION

Dioxins refer to a group of chemicals, the polychlorinated dibenzo-dioxins (PCDD), which are known to be highly toxic and chemically stable. It causes immune toxicity, reproductive effects and carcinogenicity, so it is very important to monitor and control its exposure in both industrial and residential environments [1, 2]. The most toxic PCDD isomer is 2, 3, 7, 8 tetrachlorodibenzo-p-dioxin (TCDD) and is classified as a carcinogenic component (group 1 carcinogen) to humans according to IARC. It can be formed from the combustion organic compounds in waste incinerators such as municipal waste, medical waste, army stockpiles (chemical agents), and herbicide overuse, thus TCDD removal to well below (1 ng/m^3) is generally required [3].

Since 1991, different sorbents such as activated carbon has been widely adopted for dioxin removal [4, 5]. Carbon nanotubes (CNTs), discovered Iijima in 1991, are quasi-one-dimensional nanostructures with unique thermal and electronic properties that has attracted much interest to develop for applications in nanoelectronics. It has been shown

that CNTs can detect molecules such as NH_3 , O_2 and, NO_2 in small concentrations but H_2O , H_2 , CO cannot be detected using intrinsic CNTs since they are only adsorbed weakly on the tube wall and there is almost no charge transfer between the tube and molecules [6]. To overcome these limitations, a few strategies, such as creation of defects, chemical functionalization, and heteroatom doping, were proposed to alter the chemical nature of CNTs and enhance their sensitivity and selectivity [7, 8-14]. Little information is known about the types of defects that might be introduced during nanotube synthesis, but vacancy defects, i.e., defects resulting from missing carbon atoms, are likely candidates [9-11].

Recent investigations by using temperature-programmed desorption (TPD) on multi-walled nanotube showed that CNTs have more efficient sorbent than activated carbon for dioxin removal [4]. Great efforts have been devoted to find a suitable material for efficient dioxin adsorption and detection [15-20]. Among the well-established computational techniques to study the adsorption properties of metals and CNTs, the density functional theory (DFT) calculations have been used as a standard tool for large system with reliable compromise between accuracy and efficiency [15]. Kang et al. [16] studied the dioxin

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interaction with SWCNT and metal-doped (Fe, Li and Na) graphene sheet by using DFT calculations. Using the first principle calculations, Fagan et al. [17] demonstrated TCDD adsorption on SWCNT and predicted that dioxins can be adsorbed onto the surface of the CNTs stronger than the nanotube with lattice defect. Pan et al. [18] have reported the inclusion of TCDD with β -cyclodextrin by performing quantum mechanics and molecular dynamics (MD) calculations. It was found that β -cyclodextrin may serve as a potential substrate enriching TCDD. They further studied that 1-butyl-3-methylimidazolium dicyanamide ionic liquid can be used as efficient sorbent for TCDD using combined (MD) simulation and quantum chemical (QM) calculation [19]. Zhang et al. [20] examined the binding of TCDD molecule on a graphene sheet. It was found that they can be effective adsorbents for dioxin in the presence of calcium atoms. Doubtless, the solution of this problem will come from the development of dioxin sensors based on nanostructured material such as nanowires, nanoribbons, nanotubes and another unique material that exhibit a wide band gap and has potential application [21].

In this work, we report our theoretical studies of interaction between Al-doped CNT and TCDD by using the DFT calculations. The computational details for calculating the adsorption energies and the method of construction of TCDD/nanotubes complexes are given in detail in the next section.

COMPUTATIONAL APPROACH

In this work, all calculations were performed by using the *ab initio* DFT package SIESTA, which is based on localized basis set and the method of pseudopotentials [22]. In this software the electronic wave functions are constructed by linear combination of locally-confined atomic orbitals (LCAO's) [23].

The wave functions for the valence electrons were represented by a linear combination of pseudo-atomic numerical orbitals, while core electrons were represented by improved Troullier-Martins [24] pseudopotentials. We utilized soft confinement potentials [25] to produce double- ζ polarized (DZP) basis set for all species with the confinement regions corresponding to the energy shift of 50 meV which is appropriate for evading nasty overestimation of binding [26, 27]. For all systems under consideration, all atoms were allowed to relax freely until the forces on each atom were less than $0.03 \text{ eV}\text{\AA}^{-1}$. The structural relaxations as well as total energy calculations were carried out within the Generalized Gradient Approximation (GGA)

with the exchange-correlation functional of Perdew Burke Ernzerhof (PBE) [28]. Conventional DFT functional do not take into account dispersion forces, that is, London dispersion. Thus, it is essential to choose the suitable computational approaches that should consider the correct description of long-range electron correlation to incorporate the long distance van der-Waal's interaction between the adsorbent and adsorbate. We expect that long-range dispersion interactions will play a significant role in aromatic molecules adsorption on extended carbon based systems [29-32]. The present study employs the DFT-D2 method within the PBE functional for the systems under consideration. The Brillouin zone was sampled by $1 \times 1 \times 5$ special k -points using the Monkhorst-Pack scheme for all structural configuration relaxations. Furthermore, to clarify the electronic nature of the dioxane molecule and CNTs, the Hirshfeld charge [33] analysis is computed and discussed.

To evaluate the stability of adsorbed species onto nanotubes, we calculate the binding energy, E_b , of interacting systems by using the following equation:

$$E_b = E(\text{NT/TCDD}) - [E(\text{NT}) + E(\text{TCDD})], \quad (1)$$

where $E(\text{NT/TCDD})$ is the total energy of the nanotube interacting with TCDD molecule, $E(\text{NT})$ is the total energy of the perfect nanotube and $E(\text{TCDD})$ is the total energy of an isolated TCDD molecule. In such a depiction, $E_b < 0$ corresponds to an energetically favorable configuration. The accuracy of our DFT-D2 calculations has been evaluated by state-of-the-art *first principles* method at the B3LYP level of theory.

RESULT AND DISCUSSION

First, we considered the adsorption of single TCDD molecule on the perfect (10, 0) CNT. Two possible configurations are investigated, including when the two six-member carbon rings of TCDD were parallel/perpendicular to the CNT surface (Fig.1). The geometry of the (10, 0) CNT nanotube, TCDD molecule and various configuration of CNT/TCDD complexes are optimized to find the most stable adsorption configuration. The most stable adsorption configurations in which the TCDD molecule is placed parallel to the tube axis are shown in Fig.2 (e). The calculated adsorption energy, charge transfer, and the binding distance are summarized in Table 1. After the adsorption of TCDD molecule, interaction distances between the closest atoms of the TCDD molecule and CNT is about 3.401 \AA , which are very close to the value (3.42 \AA) found in

the case of our previous study[34].The bond lengths and especially the angle between two adjacent benzene rings in TCDD molecule were altered. Besides that, the C-C bond length near the adsorbate almost remains unchanged. The corresponding binding energy is obtained to be approximately -0.52eV , which is comparable to that Ganjiet al [34]. There are is little charge (0.037 e) transferred from the tube to TCDD molecule. These small E_b values, charge transfer and large interaction distances indicate that the TCDD molecule adsorbs weakly due to van der Waals interaction CNT and TCDD[35-42].

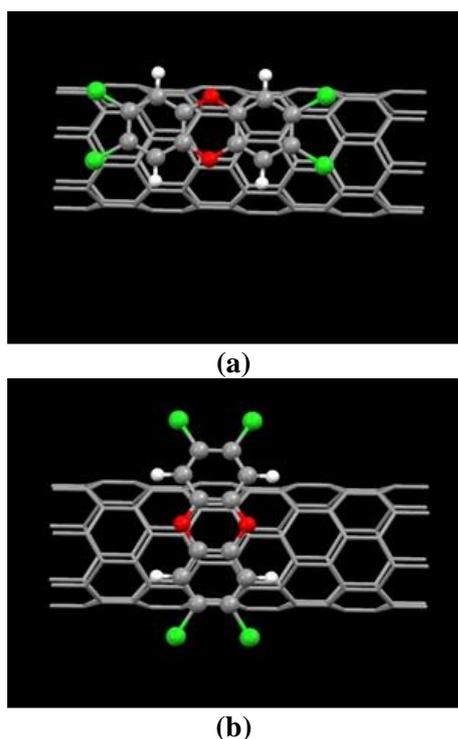


Fig. 1. Models for a TCDD molecule interacting with CNT (10, 0) with molecular axis (a) parallel and (b) perpendicular orientation to the tube axis.

There are some theoretical studies of defected CNT, showing that the formation of defected CNT was a useful way of modifying in electronic, mechanical, and adsorption properties [43-46].Hence, we studied the interaction of the defected CNT with a TCDD molecule using similar computational procedure. Among various native defects, we focused on defect, in which showed the most stable optimization structure of C-vacancy (V_C) as shown in Fig.1 (f).To investigate the TCDD adsorption on the V_C defect in (10, 0) CNT, we initially placed a TCDD molecule above a vacant site. We now consider the adsorption nature of TCDD molecule onto the V_C defect using similar computational procedure.Fig.2 (g) represents the optimized structures and calculated equilibrium distances between the two closest atoms from the two entities and angles for the adsorption of TCDD molecule. The calculated binding energy for the energetically most favorable configuration and equilibrium distance between the closest atom between V_C defect and TCDD are determined to be about -0.34 eV and 3.498 \AA , respectively. Our calculated results show that there is no enhancement of TCDD adsorption on the defected CNTs. Furthermore, after performing full structural optimization procedure for the configurations with lowest binding energy, the geometrical parameters for TCDD molecule remained almost unaltered during the adsorption process. It can be found from the calculated binding energies that in all the cases the vacancy defect in CNT caused a decrease in the interaction between the two entities in comparison to that of perfect CNT. From the above discussions, it can be obviously seen that TCDD adsorption ability of vacancy defected CNTs is weaker than that of perfect CNT. In Table 1 we listed the binding energies and equilibrium distances for the energetically most stable configurations.

Table 1: Calculated binding energies, bonding distances and charge transfers with DFT-D method for TCDD molecule interacting with perfect CNT, defected CNT, Al-CNT

Entry	System	Binding energy(eV)	$d_{A-S}(\text{\AA})$	$Q_T (e)$
1	TCDD/CNT(10,0)-Par	-0.52	3.401	-0.037
2	TCDD/CNT(10,0)-Perp	-0.35	3.502	-0.021
3	TCDD/CNT(10,0)-def-Par	-0.34	3.278	+0.131
4	TCDD/CNT(10,0)-def -Perp	-0.30	3.203	-0.019
5	TCDD+Al-dop-CNT-10,0--Cl-Cl-Par	-0.86	2.480	+0.36
6	TCDD+Al-dop-CNT-10,0--Cl-Cl-Perp	-0.55	2.623	+0.294
7	TCDD+Al-dop-CNT-10,0--C-Ring-Par	-0.62	2.968	+0.313
8	TCDD+Al-dop-CNT-10,0--C-Ring-Perp	-0.62	2.461	+0.322
9	TCDD+Al-dop-CNT-10,0--O-O-Par	-0.62	3.244	+0.331
10	TCDD+Al-dop-CNT-10,0--O-O-Perp	-0.43	3.318	+0.292

The results indicate that the average bond length of the Al-C in Al-CNT for the energetically favorable state decreased after the adsorption. In the case of TCDD molecule only the average bond length of C-Cl is slightly increased and other bond length such as C-C, C-O are decreased after adsorption on the Al-CNT. The angle between two adjacent benzene rings in TCDD molecule was also increased. A more negative E_{ad} between the Al-doped and TCDD indicates that the doping of Al in CNT can improve the reactivity of tube toward the TCDD molecule, which is in agreement with the usual mechanism that is proposed for such binding: the TCDD binds at the exposed Al atom which is electron deficient and can receive electrons from chlorine. As a result for Al-CNT system, a significant enhancement of about 65% in binding energy was observed which is significantly stronger than the pure CNT.

We also determined the electronic density of states (DOS) of the TCDD/CNT, TCDD/defected CNT and TCDD/Al-CNT complexes to fully understand the bonding nature of this TCDD through electronic structure. Fig. 5 shows the total electronic DOS for the most stable state of TCDD/CNT, TCDD/defected CNT and TCDD/Al-CNT complexes. It can be seen from the figure that

the electronic spectra near the Fermi level remained unchanged after the adsorption process. Indeed, the energy spectra for the TCDD/CNT, TCDD/defected CNT are almost the same as those for perfect CNT and no significant change can be observed on the DOS near the Fermi level upon the adsorption of TCDD molecule and corresponding CNTs.

This result emphasizes also that the adsorption of TCDD on both the perfect CNT and defected CNT does not change its structural and electrical properties. In the case of the TCDD/Al-CNT complex, however, the DOS near the Fermi level has obvious change due to adsorption of TCDD molecule. By comparing the DOS of the considered systems, we find that the adsorption of TCDD molecule leads to the additional peak pinned at the Fermi level which take part in the bonding process, as shown in Fig. 5(c). On the other hand, the difference in the Fermi level of the Al-CNT ($E_F = -4.66$ eV) and TCDD/Al-CNT ($E_F = -4.46$ eV) clearly shows a charge transfer between the Al-CNT and TCDD in the adsorption process. This result rationalizes the observation that Al dopants have a strong influence in TCDD adsorption systems.

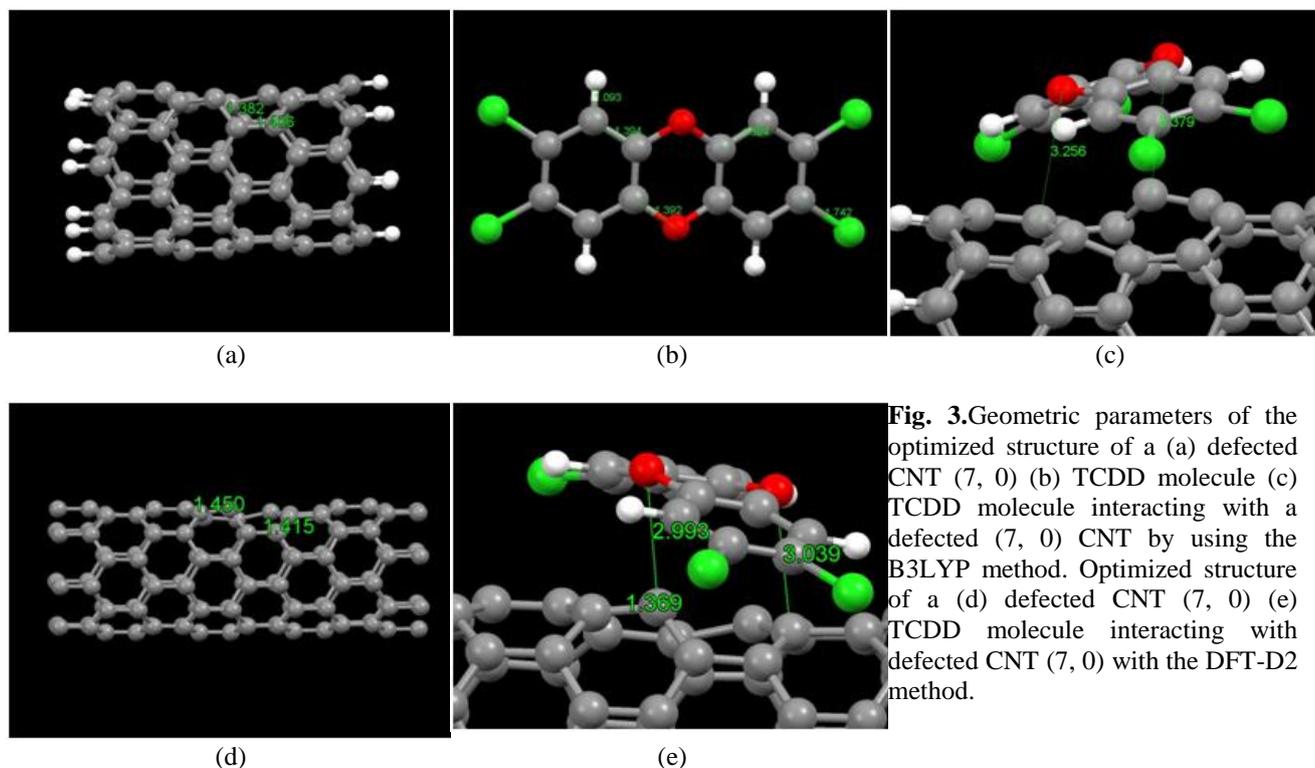


Fig. 3. Geometric parameters of the optimized structure of a (a) defected CNT (7, 0) (b) TCDD molecule (c) TCDD molecule interacting with a defected (7, 0) CNT by using the B3LYP method. Optimized structure of a (d) defected CNT (7, 0) (e) TCDD molecule interacting with defected CNT (7, 0) with the DFT-D2 method.

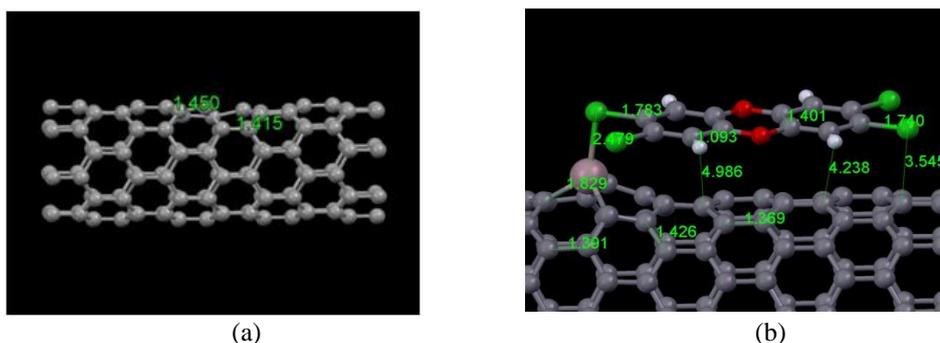


Fig.4. Schematic representation of (a) geometric parameters of the optimized Al-CNT (10, 0) and (b) energetically favorable TCDD/Al-CNT (10, 0) - complex.

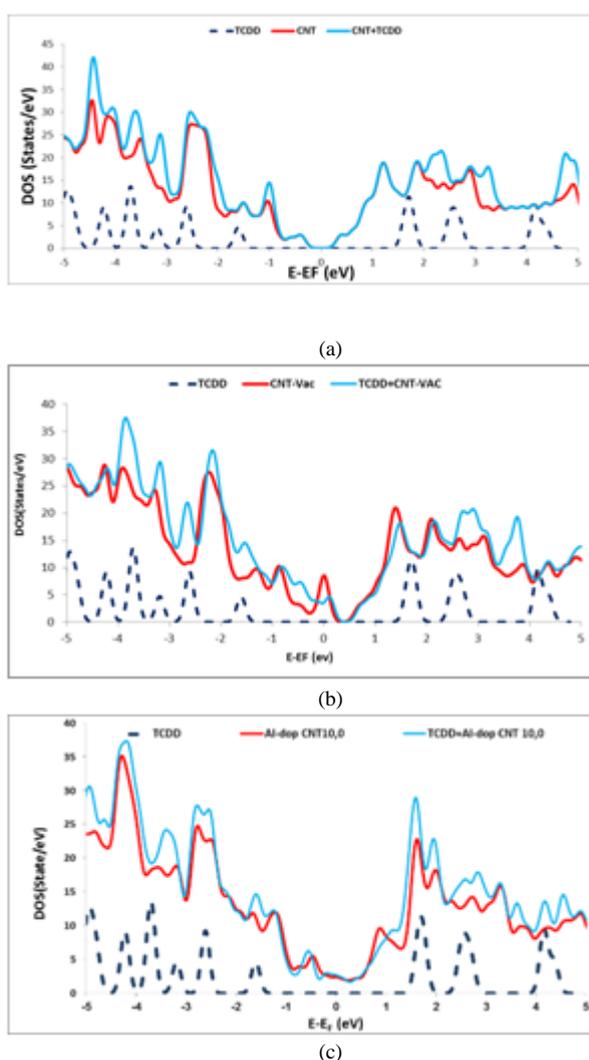


Fig. 5. Comparison between the density of states (DOS) for (a) an isolated TCDD molecule, an isolated CNT (10, 0), and the combination of the two at equilibrium geometry, and corresponding DOSs for energetically favorable (b) TCDD/CNT (10,0) with defect systems, (c) TCDD/Al-CNT(10, 0) (d) additional one peak appear above the Fermi level which take part in the bonding process TCDD/Al-CNT(10, 0)

To further investigate the change in the electronic structure in the present systems and enhancement effect of dopant on the TCDD adsorption, the charge transfer between the TCDD and Al-CNT/CNT system was calculated. Electron charge transfer plays an important role in the

electronic properties and stability of interacting systems. The charge analysis was analyzed based on Hirshfeld method which is shown to be more reliable and yield chemically meaningful charges compared to Mulliken and Bader methods [49–52]. Charge analysis indicates that about 0.36 e charge

has been transferred from the TCDD molecule to the Al-CNT while for TCDD/CNT complex about 0.03 *e* was found to be transferred from the CNT to the TCDD molecule. The enhancement in the TCDD adsorption on Al-CNT in comparison with the CNT can be explained in terms of charge analysis. This is confirmed by the Hirshfeld charge analysis, the strong binding nature of TCDD/Al-CNT complex in comparison with the TCDD/CNT system.

CONCLUSION

In conclusion, we have carried out first-principle calculations using dispersion-corrected density functional theory (DFT-D2) to investigate the adsorption of a TCDD molecule onto a CNTs. It is established that the TCDD weakly interacts with a perfect and defected CNT surface could be significantly enhanced to region of chemisorption by doping Al into structure of CNT. The doped Al induced altering in the electronic structure of CNT and facilitates adsorption of the TCDD molecule. Adsorption energies calculated from the GGA-PBE method are in good agreement with the corresponding B3LYP values. The results showed that TCDD molecule prefers to be adsorbed onto the Al-CNT with the binding energy of about -0.86 eV.

The obvious structural changes, significant binding energies and charge transfer of the TCDD/Al-CNT system reveal that it is strong interaction. The binding nature of TCDD molecule adsorbed on the CNTs surface is also investigated by the DOS analysis. Results of the electronic structure and Hirshfeld analyses indicate that in the case of TCDD/pure CNTs system there is no significant hybridization between the respective orbital but the adsorption of TCDD on the Al-CNT surface strongly suggests an orbital mixing between TCDD molecule and respected substrate near the Fermi level. Therefore, the Al-CNT would have unique application potential in chemical sensors and promising candidate for TCDD adsorption.

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