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Removal of dioxane pollutants from water by using Al-doped single walled carbon nanotubes

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Abstract:

The detection and fast enrichment of toxic organic pollutants are challenging issues in the field of environmental science. We have studied the adsorption of dioxane on perfect, defected, and Al-doped CNTs by DFT calculations adopting the vdW forces corrections (vdW-DF). The accuracy of the vdW-DF results have been evaluated against the state-of-the-art B3LYP-D3 level of theory and it was shown that there is worthy agreement between two respected methods. It was found that dioxane adsorption ability of Al-CNT is much better (stronger) than perfect and defected CNTs. Calculations of adsorption behavior of water molecule as solvent demonstrate the existence of a stronger interaction between dioxane and Al-CNT in

comparison with water molecules. Finally, we studied the interaction of dioxane molecule with CNT and Al-CNT in the presence of water molecules in ambient conditions using DFTB-MD simulation. We showed that dioxane in the presence of water molecules is weakly bound (physisorption) to the outer surface of CNTs while it can be adsorbed on the Al-CNT system stronger than the water molecules as a competitor. Our study provides molecular level understanding of the interactions between dioxane and CNTs and may be instructive for toxicity agent adsorption and detection from environment.

Keywords: Dioxane; CNT; DFT; DFTB-MD; adsorption; organic pollutants.

1. Introduction:

1, 4-Dioxane, often called dioxane, is a heterocyclic organic compound that has many industrial uses such as solvent due to its proton-accepting nature, solvent stabilizer, wetting and dispersing agent in textile process and chemical intermediate [1] It can be produced as an undesired byproduct in the polyester manufacturing process [2] On the other hand, dioxane is a known human carcinogen and exposure to high concentrations of it may cause eye, skin and respiratory irritation, nervous system effects and liver and kidney toxicity [1] So, it is very important to monitor and control its exposure in both industrial and residential environments. It is reported to be the dominant water pollutant. The dioxane standard value for drinking water was established at concentration 0.05 mg/L in 2004 [3] It is a commonly found recalcitrant organic contaminant that is increasing concern around the world, causing contamination levels to be a recent concern for scientists and engineers [1, 4]

Several research studies have been focused on the adsorption of dioxane from drinking water such as bioremediation [5] and advanced oxidation processes (AOP) [6] Furthermore, numerous works have been performed for the interaction of dioxane molecule with Pd [7], Cu [8], Ag [9], and silicon surfaces [10] Recently, various porous materials such as granular activated carbon (GAC) [11] and activated carbon [3] have been used to adsorb dioxane.

In recent years, CNTs [12] have been intensively studied due to their importance as building blocks in nanotechnology. The special geometry and unique properties of CNTs offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and biosensors, field emission display, etc. [13-16] CNTs can detect molecules such as NH₃, O₂, NO₂ in small concentrations but H₂O, H₂, CO cannot be detected using pure CNTs because of weak Van der Waals interaction between CNTs surface and molecules [17] It is considered to be promising candidates for many areas of applications including special adsorbents in water treatment and environmental remediation [13, 18-19] To the best of our knowledge, there are

no experimental and theoretical studies of dioxane molecule adsorption on CNTs. The aim of the present work is to evaluate the interaction between dioxane and CNTs by means of density functional theory (DFT) calculations. The paper is organized as follows. We first investigated the preferential adsorption geometries of dioxane-CNTs interface and analyzed the adsorption energies and electronic properties during the adsorption process. Then, the dioxane-water mixture is studied on CNT and Al-CNT in ambient conditions using molecular dynamic simulations based on the density functional tight-binding method (DFTB-MD). The computational details for calculating the binding energies and the method of construction of dioxane/nanotubes are given in detail in the next section.

2. Computational method:

All DFT calculations were performed using the *ab initio* package SIESTA, which is based on localized basis set and the method of pseudo potentials [20] In this software the electronic wave functions are constructed by linear combination of locally-confined atomic orbitals (LCAO's) [21] Norm-conserving pseudo potentials of Troullier-Martins [22] with the valence electron configurations of all considered atoms were implemented. We utilized soft confinement potentials [23] 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 [24, 25]. 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 energies calculations were carried out within the Generalized Gradient Approximation (GGA) with the exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE) [26] 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, charge transfer was calculated by counting the charge difference between the isolated and adsorbed entities.

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

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

where $E(\text{NT/diox})$ is the total energy of the nanotube interacting with dioxane molecule, $E(\text{NT})$ is the total energy of the perfect nanotube and $E(\text{diox})$ is the total energy of an isolated dioxane molecule. In such a depiction, $E_b < 0$ corresponds to an energetically favorable state.

Furthermore, we have also performed self-consistent-charge density functional based tight binding molecular dynamics (SCC/DFTB-MD) simulation of dioxane-water/CNT and dioxane-water/Al-CNT complex at ambient condition. SCC/DFTB-MD calculations have been carried out using the DFTB+ code [27-32] DFTB+ uses the DFTB method based on a third-order expansion of the Kohn–Sham total energy DFT with respect to charge density fluctuations. All of the MD calculations were performed in the canonical statistical ensemble (i.e. the thermodynamical system under consideration is described by the number of particles N , the volume V , and the temperature T as variables). The equation of motion for all MD simulations was integrated using the velocity-Verlet [33] scheme with a 1 fs time step, and the considered simulation time at a particular T was 50 ps. The structure under study is in contact with Andersen thermostat [34] having fixed temperature 300 K. The Quantum mechanics (QM) potential was calculated at every MD step using the SCC/DFTB [35-38] method which is based on some approximations to standard density-functional theory. In this work the Slater–Koster (S–K) type parameter set [35, 37-38] was implemented.

3. Result and discussion:

3.1. Adsorption properties

We first consider the adsorption of dioxane on the exterior surface of a (7, 0) CNT. As shown in Fig. 1, three initial states are considered for a dioxane molecule being bound to the CNT surface. The hydrogen and oxygen atoms of dioxane are situated above the surface in the first configuration (Fig. 1 (a)). In the second configuration the hydrogen atoms are positioned over the sidewall of tube while the dioxane ring is perpendicular with respect to the tube surface (Fig. 1 (b)). The system includes 84 C atoms and one dioxane molecule. The optimized CNT and dioxane molecules (Figs. 1 (c) and (d)) were used for the molecule adsorption. Full structural optimization procedure has been carried out for all the selected configurations and then the binding energies were estimated. As shown by comparison of the calculated binding energies (Table 1), the dioxane molecule prefers to be adsorbed through its H and O atoms (see Fig. 1 (a)). The calculated binding energy for the energetically most favorable configuration and the equilibrium distance between the closest atoms between the CNT and the dioxane are about -0.50 eV and 2.990 Å, respectively. Our *first-principles* calculation results show also that the bonds length in dioxane and nanotube do not vary upon adsorption (the C–O and C–H bonds length changes from 1.436 and 1.107 Å to 1.437 and 1.108 Å, respectively). The relatively far equilibrium distance between the adsorbed dioxane molecule and the CNT surface and the obtained binding energy, all indicate weak interaction (physisorption) between dioxane and CNTs [39-41]. Further information of the structural geometries of the isolated and adsorbed dioxane molecule onto the CNT is represented in Fig. 1.

We have also calculated the binding energy using standard DFT method (without the vdW correction) to examine the effect of vdW forces on the adsorption properties. The optimized CNT and dioxane molecules with the standard DFT method were used for the molecule adsorption. The calculated binding energy and equilibrium distance are estimated to be about -0.40 eV and 3.320 Å, respectively, which reveals that vdW forces don't play important role in binding energy estimation of system under study.

We next evaluate the accuracy of the vdW-DF results against the state of the art high level quantum chemistry method at the B3LYP-D3/def2-TZVP [42] level of theory. After full structural optimization of the considered systems, the result shows that dioxane molecule can be adsorbed on the exterior sidewall of H-capped (7, 0) CNT with binding energy and equilibrium distance of -0.51 and 2.96 Å, respectively (Fig. 1 (g)). All calculations, including full structural optimization and binding energy estimation, were performed with the ORCA code (the program with a modern electronic structure package) [42]. These findings indicate the reliability of present vdW-DF method in adsorption properties evaluation.

We have also calculated the adsorption of dioxane molecule onto a large diameter (low curvature) CNT to consider the effect of curvature on the adsorption nature. For adsorption properties analysis using the vdW-DF method, we have considered two configurations for a dioxane molecule approaching to the exterior surface of a (10, 0) CNT (Fig. 2). After full structural optimization of the considered systems, we found that dioxane molecule bounds to the surface of CNT (10, 0) with binding energy and equilibrium distance of about -0.27 eV and 2.950 Å, respectively. The binding energy and binding distance demonstrate that physisorption takes place between dioxane and the CNT (10, 0). The results indicate that the average bond length of the C-C in the CNT (10, 0) and also the C-O and C-C bonds length of dioxane remain unchanged after adsorption. The details of bonds length and angles are shown in Fig. 2. Comparing the obtained results indicates that the binding energy of dioxane increases for adsorption onto the higher curvature CNTs.

To examine the role of structural defects in adsorption behavior of dioxane molecule on the outer surface of the nanotube, we have considered a vacancy defect in a (10, 0) CNT as can be seen in Fig. 2. To find the most favorable adsorption configuration, a dioxane molecule is initially placed at different positions above the defected CNT surface. The adsorption sites are generally divided into three categories, the hydrogen atoms are positioned with a parallel or

perpendicular orientations in the first and second configurations (Fig. 2 (e), (f)) while in the third one, the O and H atoms of dioxane situated above the surface (Fig. 2 (g)). The obtained results show that dioxane molecule prefers to be adsorbed through the O and H atoms onto the defected nanotube. The obtained binding energies for the defected CNT interacting with the dioxane molecule are tabulated in Table 1. The result of full structural optimization shows that the bonds length of two interacting entities differs quite a bit after adsorption. The calculated binding energy and equilibrium distance are about -0.13 eV and 2.83 Å, respectively. The binding energy and distance of molecule/defected CNT reveal that there is weak interaction between defected CNTs and dioxane in adsorption. The obtained binding energy of other considered states after full structural optimization is estimated to be about -0.1 eV. It can be seen from comparison of the calculated binding energies for dioxane on the considered perfect CNT and defected CNT that the binding energy of dioxane on perfect CNTs is slightly higher (stronger) than that on the defected counterpart. Indeed, the slightly higher binding energy indicates that capability of perfect CNTs in dioxane adsorption is rather better than that of defected one.

In this section, we study the adsorption of dioxane molecule on Al-doped CNT (10, 0) (Al-CNT) surface in the various adsorption sites. In the starting configuration, the oxygen atoms of dioxane situated over the Al atom of the surface (Fig. 3 (a)) while in the second one the hydrogen atoms are positioned over it (Fig. 3 (b)). After full geometry relaxation, the E_b value and corresponding structural parameters for adsorbed dioxane molecule on the Al-CNT system were calculated. Our *first-principles* results show that dioxane prefers to be adsorbed on the Al-CNT via its O active site. The binding energy for the energetically favorable configuration and the equilibrium distance between the closest atoms are determined to be -1.42 eV and 1.95 Å, respectively (Fig. 3 (a)). It was clearly found that the binding energy was enhanced for the energetically most favorable state of this system. As a result, for Al-CNT system, a significant

enhancement of about 80% in binding energy was achieved, which is significantly stronger than the pure CNTs. Thus, the higher binding energy and shorter bonding distance of this system in comparison with the perfect and defected CNTs reveals strong adsorption of dioxane by Al-CNT system.

We now compare the adsorption behavior of water molecules on CNTs as solvent to dioxane. As shown in Fig. 4, two sites are considered for a H₂O molecule attached to the exterior surface of a (10, 0) CNT. Full structural optimization procedure has been carried out for all configurations of the considered systems and then the binding energies were calculated. As shown by comparison of the binding energies in Table 1, H₂O molecule prefers to be adsorbed through the O active site. The calculated binding energy for the energetically most favorable configuration, the equilibrium distance between the closest atoms and charge transfer between two interacting system (Table 1) are about -0.25 eV, 3.35 Å, and 0.08 *e*, respectively. Our vdW-DF results are in agreement with other theoretical studies [48, 49]. The binding energy, large equilibrium distance and amount of transferred charge all indicate weak interaction (physisorption) of water molecule with CNTs.

We have further considered the interaction between a H₂O molecule and Al-CNT system in two adsorption sites (O atom and H atoms approaching to the Al atom of the Al-CNT). The calculated E_b values and the corresponding equilibrium distance between the closest atom between Al-CNT and H₂O for the energetically favorable configuration are estimated to be about -1.10 eV and 2.006 Å, respectively (Fig. 4 (d)). We found that a significant enhancement in binding energy was observed for Al-CNT in H₂O adsorption which is significantly stronger than the perfect CNT. Our findings, surprisingly, reveal that dioxane adsorption by Al-CNT is stronger than water molecule which make this nanostructured material a superior material for dioxane adsorption and removal from water.

3.2. Electronic structures

To further understand the binding nature of the present systems and enhancement effect of dopant on the dioxane adsorption, the charge transfer between the dioxane and Al-CNT/CNT system was also carried out. 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 [43] which is shown to be more reliable and yield chemically meaningful charges compared to Mulliken and Bader methods [44-47]. Charge analysis shows that about $0.35 e$ charge has been transferred from the dioxane molecule to the Al-CNT while for dioxane/CNT complex about $0.05 e$ was found to be transferred from the CNT to the dioxane molecule. The enhancement in the dioxane adsorption on Al-CNT in comparison with the CNT can be explained in terms of charge analysis. Hirshfeld charge analysis confirms the strong binding nature of dioxane/Al-CNT complex in comparison with the dioxane/CNT system.

In order to investigate the effect of dioxane/H₂O adsorption on the CNT/Al-CNT system we next calculate and analyze the density of states (DOS) for the considered systems. Fig. 5 shows the total electronic DOS for the most stable state of dioxane/CNT and dioxane/Al-CNT systems (calculated DOS for dioxane/defected CNT, H₂O/CNT and, H₂O/Al-CNT systems are given in supplementary materials). It can be seen from the spectra that the DOS of the combined system of the dioxane/CNT, H₂O/CNT and also the dioxane/defected CNT complexes are almost exactly the superposition of the DOS of the individual parts. This finding indicates that only a weak interaction exists between the dioxane and the corresponding CNTs and hence no significant hybridization between the respective orbitals of the two entities takes place. This result emphasizes also that the adsorption of dioxane on both the perfect and defected CNT does not change its electrical properties. In the case of the dioxane/Al-CNT complex, however, the DOS near the Fermi level has obvious change due to adsorption of the dioxane molecule. By comparing the DOS of the considered systems, we find that the adsorption of dioxane molecule leads to the additional one peak appear above the Fermi level

which take part in the bonding process. On the other hand, the significant difference in the Fermi level of the Al-CNT ($E_F = -4.69$ eV) and dioxane /Al-CNT ($E_F = -4.33$ eV) clearly shows a charge transfer between the Al-CNT and dioxane in the adsorption process. In the case of H₂O/Al-CNT complex the significant difference in the Fermi level of the Al-CNT ($E_F = -4.69$ eV) and H₂O/Al-CNT ($E_F = -4.4$ eV) clearly shows a charge transfer between the Al-CNT and H₂O in the adsorption process. On the other word, the adsorption of dioxane/H₂O molecule in the Al-CNT surface strongly suggests an orbital mixing between H₂O/dioxane molecule and Al-CNT near the Fermi level.

3.3. Atomistic simulation at aqueous media

Finally, we have performed density functional based tight-binding molecular dynamics (DFTB-MD) simulation for dioxane molecule in the presence of water molecules under ambient conditions. For this propose we considered both the dioxane-water/CNT and dioxane-water/Al-CNT systems. We have further investigated the binding nature of these complexes as well as the corresponding geometries in aqueous solution at ambient condition. The system includes a CNT (10, 0) surrounded by 96 water and two dioxane molecules. Fig. 6 represents structural parameters calculated by the DFTB-MD simulation at 298 K. The average equilibrium distance between the closest atoms between the dioxane and CNT ($d_{H...C}$) after 50 ps is estimated to be about 2.153 Å (Fig. 6 (b)). To examine the stability of system under consideration, we calculated the total energy of respected system and the result shows that it decreases at the beginning stage of the simulation and then fluctuates around -19060 eV which indicates that the system is stabilized within the simulation times (see Fig. 6 (c)). Fig. 6 (c) shows the distance between closest C atom of CNT and H atom of dioxane molecule versus simulation time in which the curve ($d_{H...C}$) fluctuates around the 2.270 Å. Our quantum mechanical based MD simulation showed that the dioxane floats to the nanotube surface and the aqueous solution affects a little on the geometries of the dioxane molecule while significantly on the equilibrium

distance between dioxane and CNT surface. Indeed, it was observed that dioxane bound closer to the CNT surface due to the solvent effect.

Furthermore, we investigated the interaction between dioxane/water and Al-CNT using the DFTB-MD simulation for 50 ps. The initial configuration for dioxane-water/Al-CNT system is demonstrated in Fig. 6(d). The results relating to the total energy of the present system for 50 ps are calculated and shown in Fig. 6(e). As can be clearly seen from the figure, the total energy of system was initially reduced and then it remains constant over time (fluctuates around -19028 eV) indicating that the system is stable in water media. We found that dioxane was adsorbed on the Al-CNT surface in competition with water molecules and a new bond forms between the dioxane and the Al atom after 14 fs. To clearly identify the adsorption of dioxane-water on the Al-CNT surface, we have examined the time evolution of distance between the dioxane and the Al atom ($d_{O\dots Al}$) in adsorption process. The results relating to these distances are shown in Fig. 6(f). Obviously, except for the obvious instability in beginning period the curve of $d_{O\dots Al}$ basically fluctuate around the 1.90 Å indicating that the dioxane stably interacts with the Al-CNT in the presence of water molecules. Comparison of the vdW-DF result in gas phase and the DFTB-MD simulation in aqueous solution shows that the average equilibrium distance between the closest atom of dioxin and Al in solvent is almost the same as the gas phase one (~1.90 Å). From the obtained results based on DFT level of theory we can expect that Al-CNT can be suitable candidate for the adsorption and remediation of dioxane in aqueous solution.

Conclusion:

Considering the unique properties and wide applications of CNTs, we have investigated the interaction of dioxane with pristine CNT, defected CNT and Al-doped CNT by using the *ab initio* vdW-DF calculations. Main attention has been paid to obtain the geometrical structure and the corresponding binding energies of the considered systems. Furthermore, we have

evaluated the accuracy of the vdW-DF results against the state of the art high level quantum chemistry method at the B3LYP-D3/def2-TZVP level of theory. The effect of adsorbed dioxane molecule onto the selected carbon based nanostructures on the electronic properties of nanotubes was also investigated. The results showed that dioxane molecule prefers to be adsorbed onto the Al-CNT with the binding energy of about -1.42 eV and charge transfer of $0.08 e$. The obvious structural changes, significant binding energies and charge transfer of the dioxane/Al-CNT system revealed that it is strong interaction between two entities. The binding nature of dioxane molecule adsorbed on the selected CNTs surface was also investigated by the DOS analysis. The adsorption of dioxane on the Al-CNT surface strongly suggests an orbital mixing between dioxane molecule and respected substrate near the Fermi level.

We have further studied the interaction between dioxane molecule and CNT/Al-CNT in aqueous environment by using the DFTB-MD simulation under ambient condition. Our *first-principles* results demonstrated the possibility of strong interaction between dioxane and Al-CNT in both gas phase and solvent. The obtained results indicated that Al-CNT seems to be suitable candidate for dioxane adsorption and remediation in aqueous solution and may be beneficial to the relevant experimental researches.

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Captions to Tables and Figures:

Table 1: Calculated binding energies, bonding distances and charge transfers (positive sign indicates the charge transfer from the adsorbate to substrate and *vice versa*) with vdW-DF method for dioxane and H₂O molecules interacting with perfect CNT, defected CNT and Al-CNT.

Figure 1: Geometric parameters of the optimized structure of a dioxane molecule interacting with a (7, 0) CNT via its (a) O and H atoms and (b) H active site and optimized structure of a (c) CNT (7, 0) (d) dioxane molecule with the vdW-DF method. Optimized structure of a (e) H-capped CNT (7, 0), (f) dioxane molecule and (g) dioxane molecule interacting with H-capped CNT (7, 0) via its O and H atoms by using the B3LYP method.

Figure 2: Schematic representation of optimized structure for a dioxane molecule interacting with a (10, 0) CNT via its (a) O and H atoms and (b) H active site. Optimized structure of a (c) CNT (10, 0) and (d) defected CNT (10, 0) and dioxane molecule interacting with a defected CNT via its H atoms with (e) parallel, (f) perpendicular orientation to the tube axis and (g) approaching via its O and H atoms.

Figure 3: Schematic representation of optimized geometry of a dioxane molecule interacting with Al-CNT (10, 0) system via its (a) O atom and (b) H atoms with the vdW-DF method.

Figure 4: Optimized geometry of a H₂O molecule interacting with a CNT (10, 0) via its (a) H and (b) O active sites. Geometric parameters of the optimized structure for the energetically favorable configuration of a H₂O molecule interacting with the Al-CNT (10, 0) via its (a) O and (b) H active sites.

Figure 5: Comparison between the density of states (DOS) for (a) an isolated dioxane molecule, an isolated CNT (10, 0), and the combination of the two at equilibrium geometry, and (b) corresponding DOSs for energetically favorable dioxane/Al-CNT (10, 0) system.

Figure 6: (a) Models for dioxane-water/CNT system at 300 K and 0 ps. (b) the total energy of dioxane and CNT in water solvent versus simulation time. (c) Time evolution distance between C and H atom of dioxane ($d_{C.....H}$) for dioxane-water/CNT system. Corresponding (d) initial configuration, (e) total energy and (f) time evolution distance between Al atom and O atom of dioxane ($d_{Al.....O}$) for dioxane-water/Al-CNT system.

Table 1:

Entry	Configuration	E_{ads} (eV)	$d_{\text{A-S}}$ (Å)	Q_{T}
1	Diox/Al-CNT(10, 0)-O-H	-1.42	1.95	+0.35
2	Diox/Al-CNT(10,0)-CH	-1.13	2.00	+0.45
3	Diox/CNT (10,0)-O-H	-0.27	2.95	-0.05
4	Diox/CNT (10,0)-CH	-0.17	2.99	-0.06
5	Diox/CNT (10,0)-vac-O-H	-0.13	2.82	-0.05
6	Diox/CNT (10,0)-vac-CH-par	-0.09	2.85	-0.08
7	Diox/CNT (10,0)-vac-CH-perp	-0.10	3.02	-0.09
8	Diox/CNT (7,0)-O	-0.4	2.99	-0.03
9	Diox/CNT (7,0)-CH	-0.08	2.98	-0.06
10	H ₂ O/Al-CNT(10, 0)-O	-1.1	2.006	+0.32
11	H ₂ O/Al-CNT(10, 0)-H	-1.03	2.027	+0.31
12	H ₂ O/CNT(10, 0)-O	-0.21	3.34	+0.02
13	H ₂ O/CNT(10, 0)-H-H	-0.2	2.59	-0.08

Fig. 1

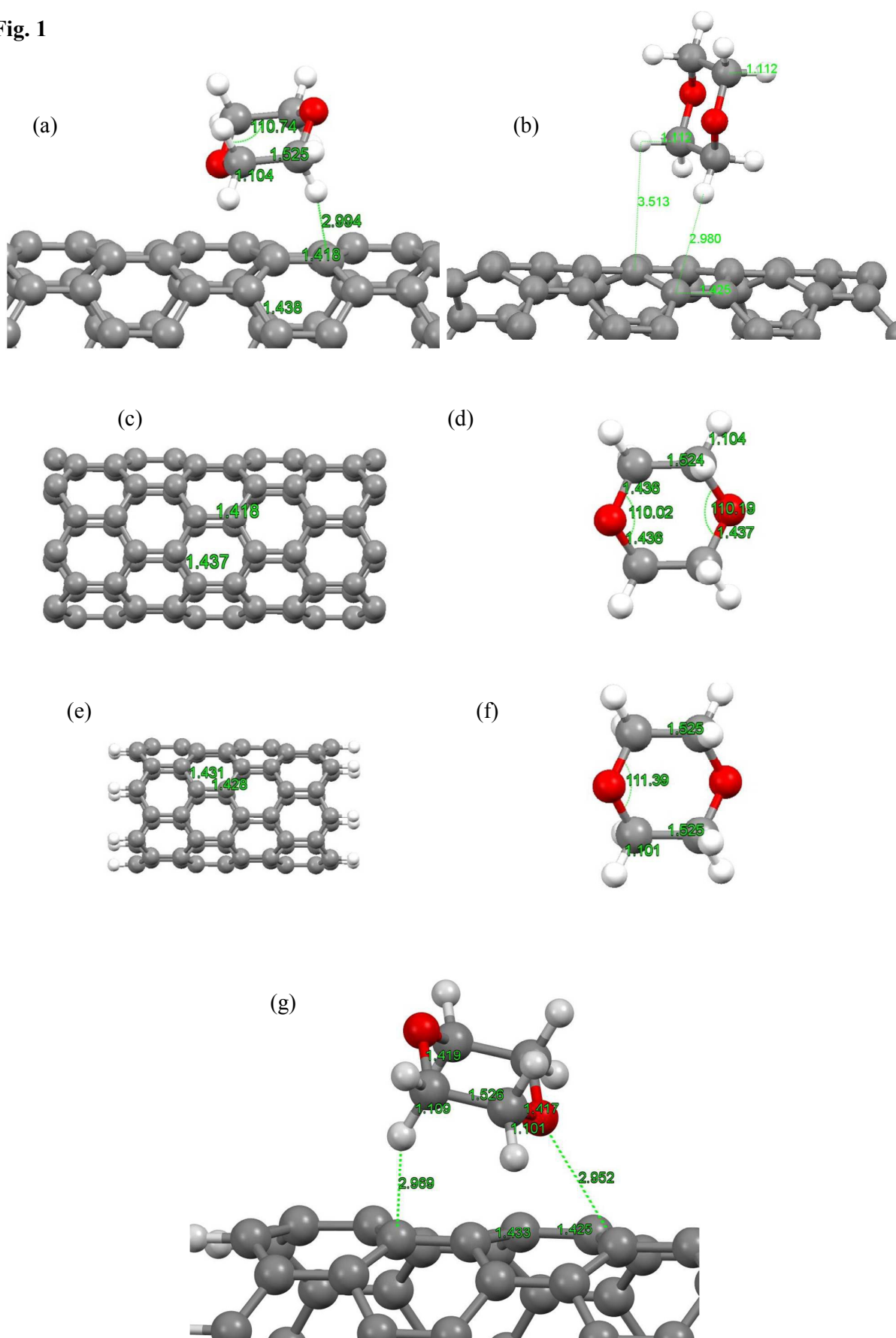


Fig. 2

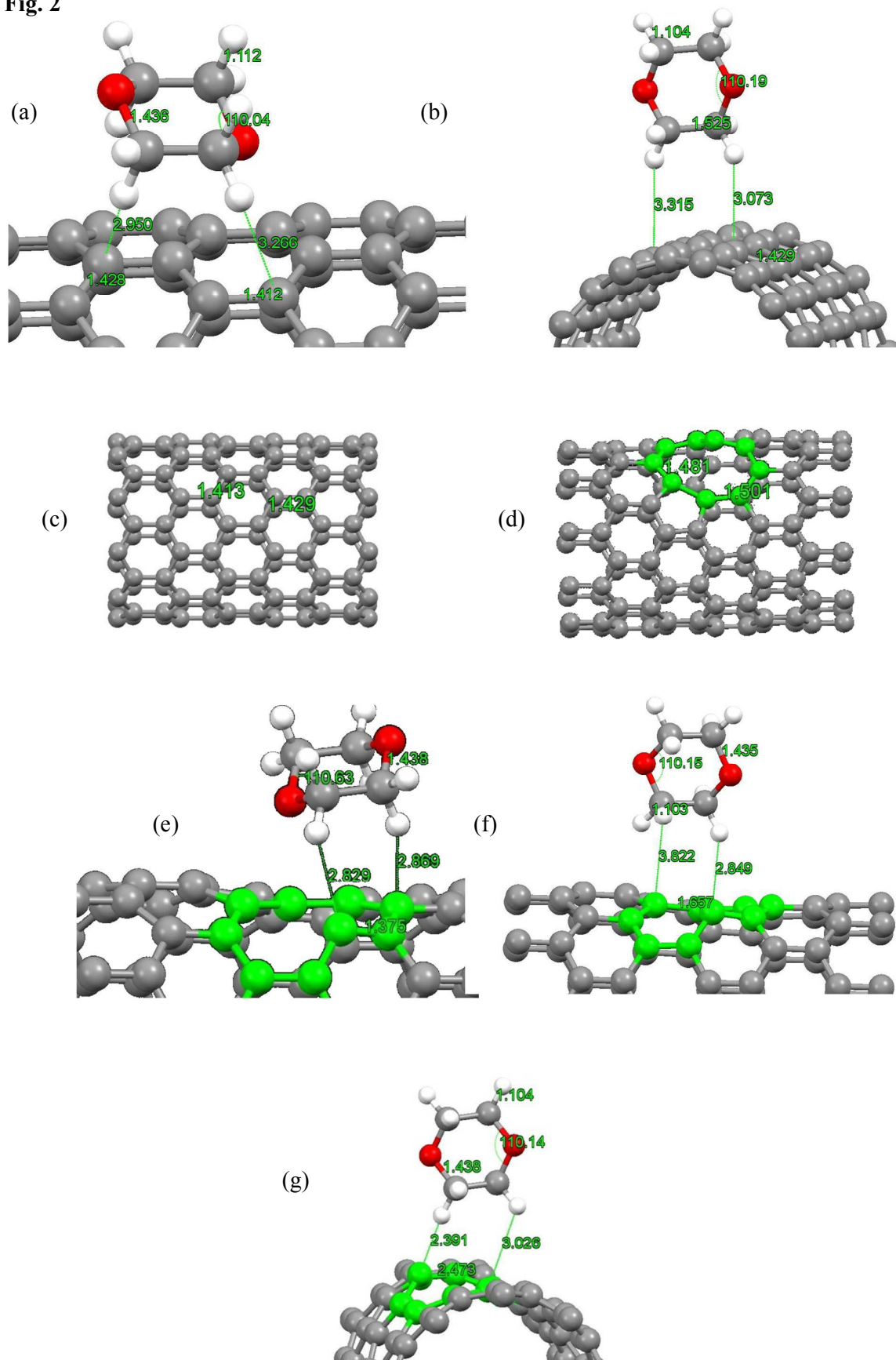


Fig. 3

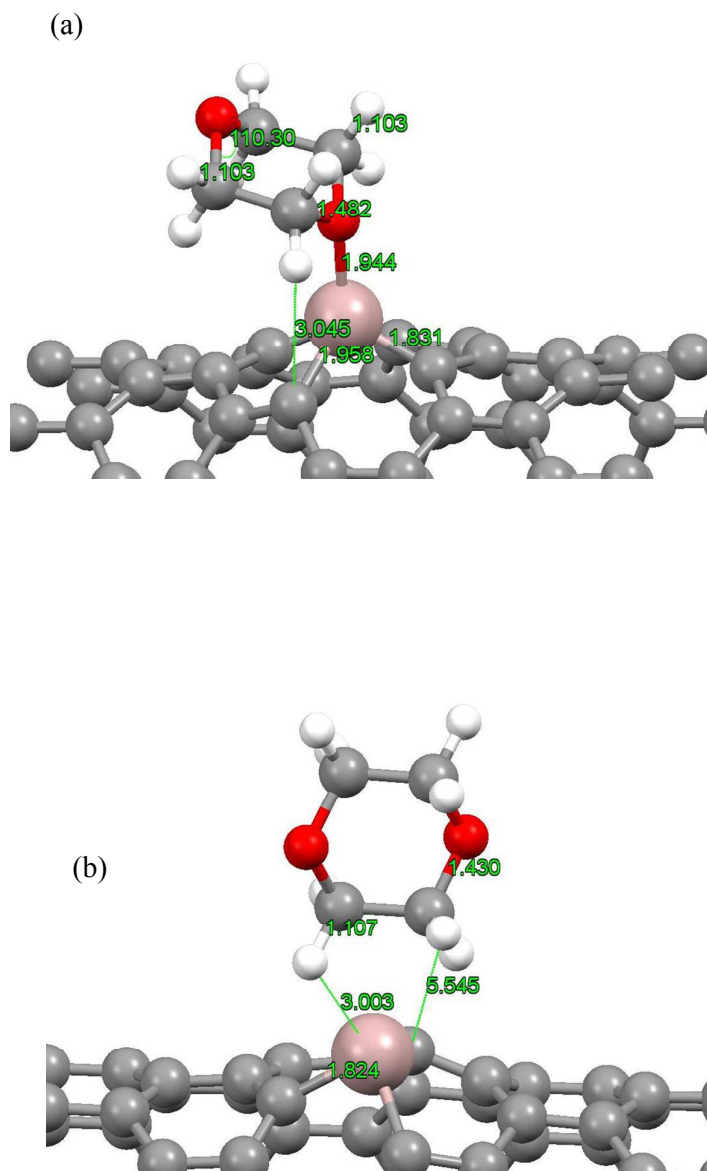


Fig. 4:

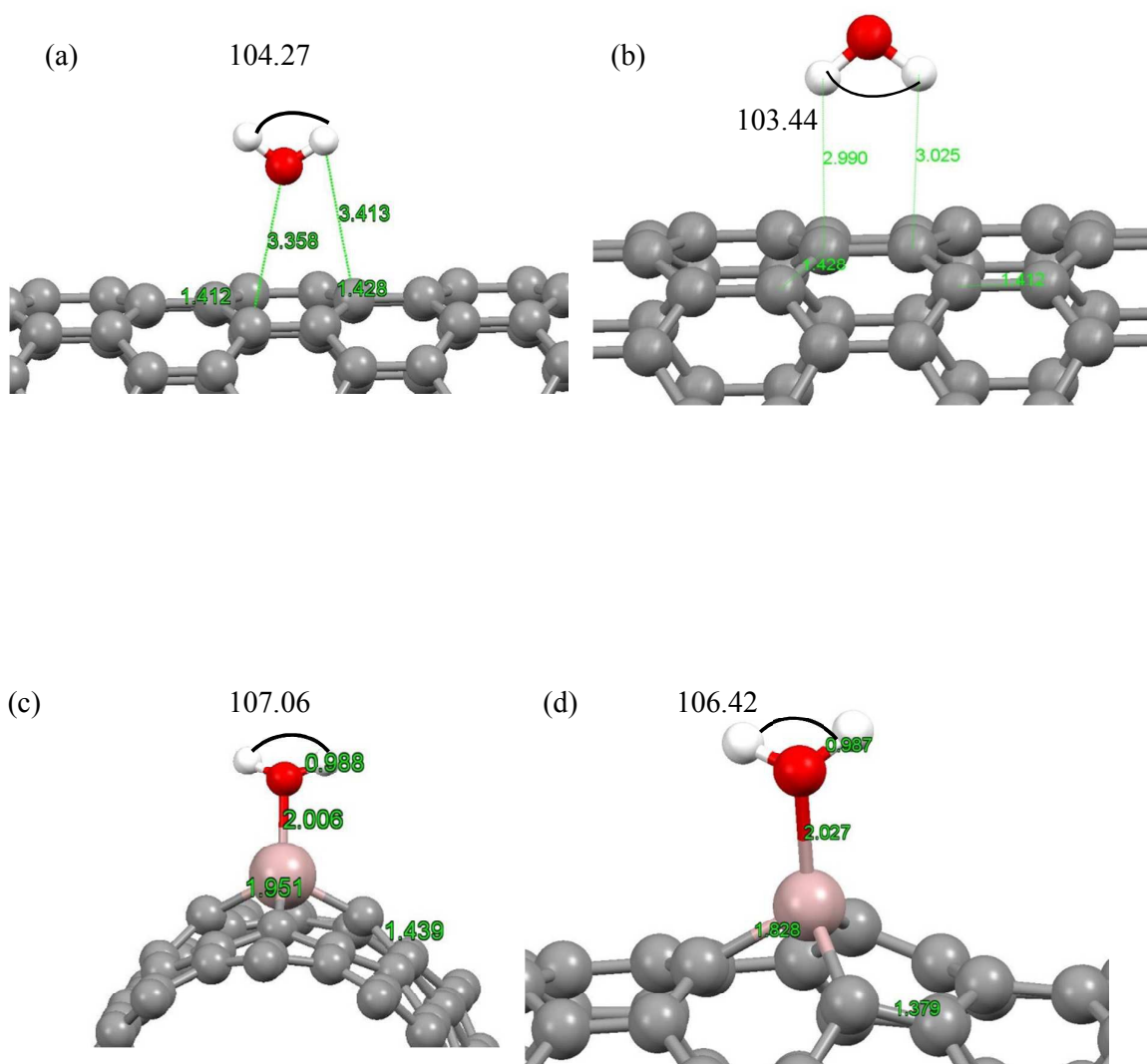


Fig. 5

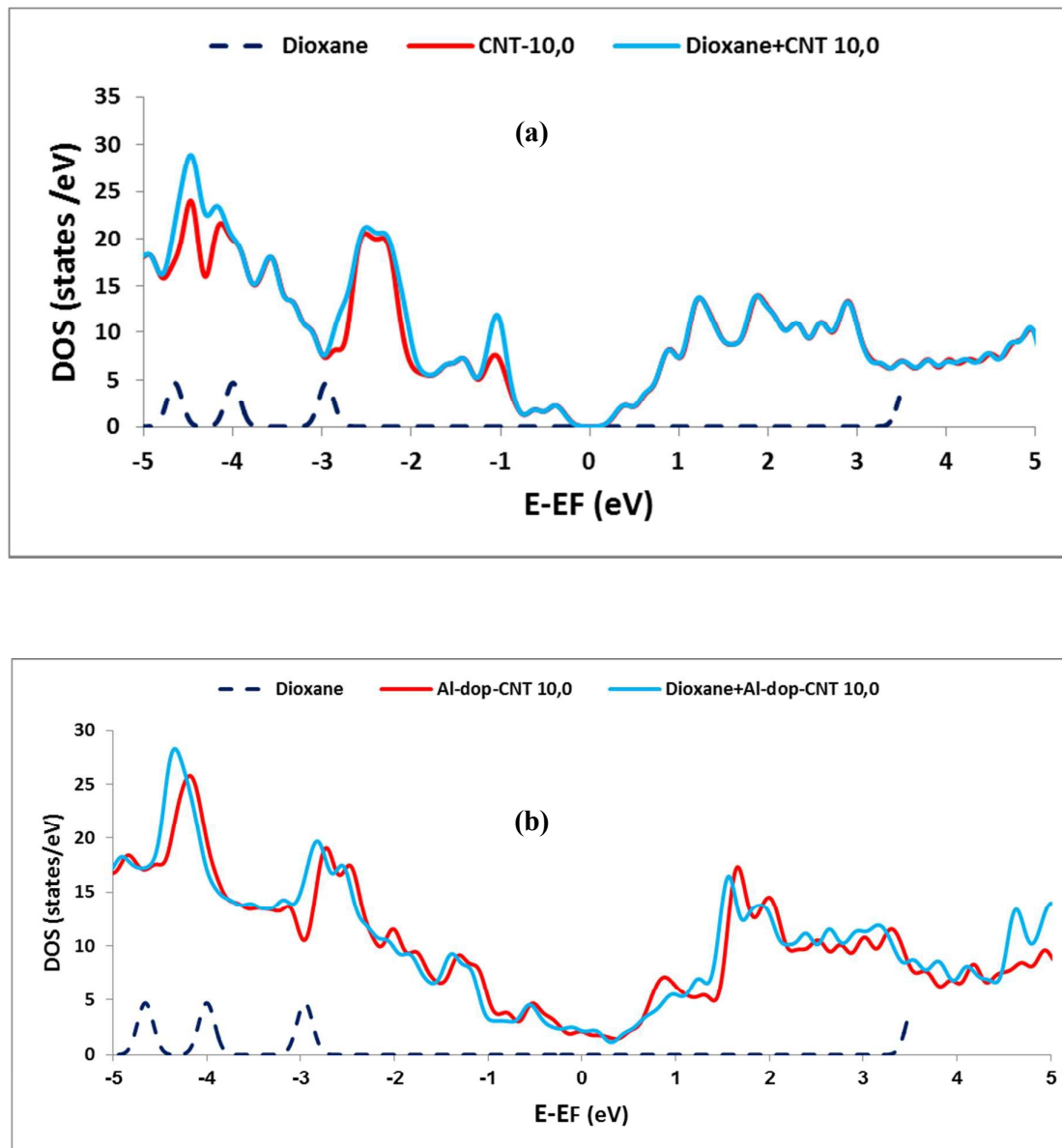


Fig. 6

