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Toluene adsorption on C_{24}, Si-doped C_{24}, and C_{20} fullerenes

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ABSTRACT

The absorption feasibility of toluene molecule in the C_{24}, Si-doped C_{24}, and C_{20} fullerenes has been studied based on calculated electronic properties of those fullerenes using Density functional Theory (DFT). It is found that energy of toluene adsorption upon the pure and Si-doped C_{24} fullerenes were in range of -1.80 and -15.72 kJ/mol with slight changes in their electronic structure. The results showed that the C_{24} and Si-doped C_{24} fullerenes cannot be used as a chemical adsorbent or sensor for toluene molecule in nature. Also, silicon doping cannot significantly modify both the adsorption energy and electronic properties of C_{24} fullerene to toluene. On the other hand, toluene molecule exhibits a high sensitivity upon C_{20} fullerene, so that the energy gap of the fullerene is changed about 91.21% after the adsorption process. We concluded that the C_{20} fullerene can be served as a reliable material for toluene detection.

KEY WORDS: C_{24} AND C_{20} FULLERENE, TOLUENE, SENSOR, DFT STUDY

INTRODUCTION

Toluene, a kind of important volatile organic compound (VOC), is used in many kinds of industries, such as painting, printing, coating, automotive, and petrochemical industries. Emission of the toluene from these industries causes air pollution and the environment, odor problem, flammability problem and affects human health. Due to these toxicological effects, air contaminated with toluene needs to be treated before it can be released to atmosphere. Therefore, adsorption and detection of toluene molecule has high importance in environmental systems, (Chang et al 2000, Vandenbroucke et al 2011).

In recent years, a wide variety of investigations have been done upon the adsorption of toluene. For example, the adsorption of toluene on ZSM5 and mordenite zeolites modified with Cs was investigated both theoretically and experimentally. Toluene removal by oxidation reaction in spray wet scrubber has been also studied. It has been shown that the highest toluene removal efficiency

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was of 91.7%. Their results showed that the sequence to prepare the catalyst affected the adsorption and plasma catalytic of adsorbed toluene, (Chungsiriporn et al 2006, Serra et al 2012 and Qin et al 2016).

After the synthesis of fullerene C60 by Kroto et al (1985) fullerenes have attracted great interest because of their physical and chemical properties and applications in nanomaterials and biomedical science, (Akasaka and Nagase 2002 and Muthukumar and Larsson 2008). Also, they play a fundamental role in medical sciences, chemistry, biology, materials, electronics, and related fields (Senapati et al 2004, Yoon et al 2009, Chamberlain et al 2011).

Among the smaller fullerenes, C20 and C24 fullerenes are a favorable candidate for examining in molecule electronic devices, nanotechnology, and biomedical engineering. Liang Xu et al (2012) have studied the interaction between empty C24 fullerene and the smallest amino acid (glycine). Their results showed that the glycine molecule is energetically favorable to interact on the C24 fullerene through the amino nitrogen active site. Also, orientation effects on the electronic transport properties of C24 fullerene were studied by Wen-Kai Zhao et al (2013) between the electrodes (Au–C24–Au). Their findings showed the application of the C24 fullerene in the field of single molecular devices or nanometer electronics. Prinzbach et al (2000) have synthesized C_{20} fullerene by using $C_{20}H_{20}$. They replaced the hydrogen atoms with bromine atoms, and then debrominated to produce C_{20} fullerene in gas phase.

An et al (2011) have tried to stabilize the highly perfect I_h symmetry C_{20} fullerene cage by placing interstitial atoms at the center of the fullerene using first-principles density functional theory (DFT). They was also investigated the transport properties of C_{20} fullerene and the endohedral $Li@C_{20}$ metallofullerene coupled to three-dimensional electrode system using DFT methods . Using different DFT methods, the transformation processes from the physisorption state to the chemisorption state of a H_2 molecule in C_{20} fullerene and B-doped fullerene $C_{19}B$ system was investigated.

In previous study, we have studied the chemical functionalization of C_{20} fullerene with NO_2 molecule. In summary, there are few studies on the C20 and C24 fullerenes and further study on the structures is of important duties. On the other hand, the doped C_{20} and C_{24} fullerenes show dramatic changes in electronic properties with respect to their pristine. Therefore; the aim of this study was to investigate the ability of toluene adsorption onto C_{24}, Si-doped C_{24}, and C_{20} fullerenes, to determine whether the fullerenes are applicable for filtering or sensing toluene molecule (An et al., 2010, Tian et al 2011 and Baei 2013).

COMPUTATIONAL METHODS

In this study, the adsorption of toluene on the C_{24}, Si-doped C_{24}, and C_{20} fullerenes are considered. C_{24} fullerene with a D_6d symmetric form consisting of two 6-membered rings joined by twelve 5-membered rings and C_{20} fullerene with an I_h symmetric form consisting of 12 pentagons and 30 bonds are selected for this purpose. DFT calculations at the level of B3LYP (Becke 1993), with the standard 6-31G* basis set were carried out on the C_{24}, Si-doped C_{24} fullerenes and the PBE (Perdew and Ernzerhof,1996) level in GAMESS package, (Schmidt et al 1996) with the standard 6-31G* basis set were performed on the C_{20} fullerene. For the C_{20} fullerene, the PBE functional show better results with respect to B3LYP method of (Perdew and Ernzerhof, 1996). These methods were used to calculate the adsorption energy (E_{ad}) of toluene on the surface of the fullerenes using the following equations:

$$E_{ad} = E_{\text{toluene/C24}} - [E_{\text{C24}} + E_{\text{toluene}}] + \delta_{\text{BSSE}} \quad \text{Eq. (1)}$$

$$E_{ad} = E_{\text{toluene/Si-doped C24}} - [E_{\text{Si-doped C24}} + E_{\text{toluene}}] + \delta_{\text{BSSE}} \quad \text{Eq. (2)}$$

$$E_{ad} = E_{\text{toluene/C20–}} [E_{\text{C20}} + E_{\text{toluene}}] + \delta_{\text{BSSE}} \quad \text{Eq. (3)}$$

Where $E_{\text{toluene/C24}}$ and $E_{\text{toluene/C20}}$ are the total energy of complex of adsorbed toluene on the C_{24} and C_{20} fullerenes. E_{C24}, EC_{20}, and E_{toluene} are the total energy of the pure C_{24} and C_{20} fullerenes and toluene molecule. $E_{\text{toluene/Si-doped C24}}$ is the total energy of complex of adsorbed toluene on the Si-doped C_{24} fullerene. $E_{\text{Si-doped C24}}$ is the total energy of Si-doped C_{24} fullerene, and δ_{BSSE} is the BSSE correction. The negative values of E_{ad} reveal that the adsorption is exothermic. For the structures, the geometry optimization, natural bond orbital (NBO) density of states (DOS), energies, and frontier molecular orbital (FMO) were calculated according to Glendening et al (1998). The energy gap (E_g) of the optimized structures was obtained by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest un-occupied molecular orbital (LUMO). Also, Fermi level energy (E_{FL}) and work function (Φ) of the considered structures are calculated.

RESULTS AND DISCUSSION

The optimized structure of C_{24}, Si-doped C_{24}, and C_{20} fullerenes are shown in Fig. 1. The C-C bond lengths of pure C_{24} and C_{20} fullerenes are in the range of 1.36-1.53 and 1.44-1.51 Å. The electronic property analysis based on DOS shows a HOMO-LUMO gap (E_g) of 1.82, 1.63, and 0.74 eV for the C_{24}, Si-doped C_{24}, and C_{20} fullerenes, respectively. E_g of the C_{24} and C_{20} fullerenes are very

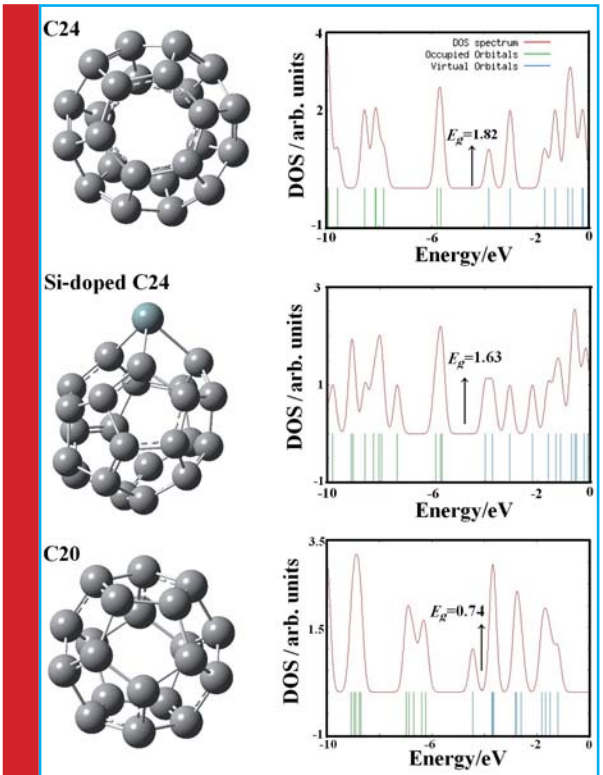

FIGURE 1. Optimized Structures of C_{24}, Si-doped C_{24}, and C_{20} fullerenes and their density of states (DOS).

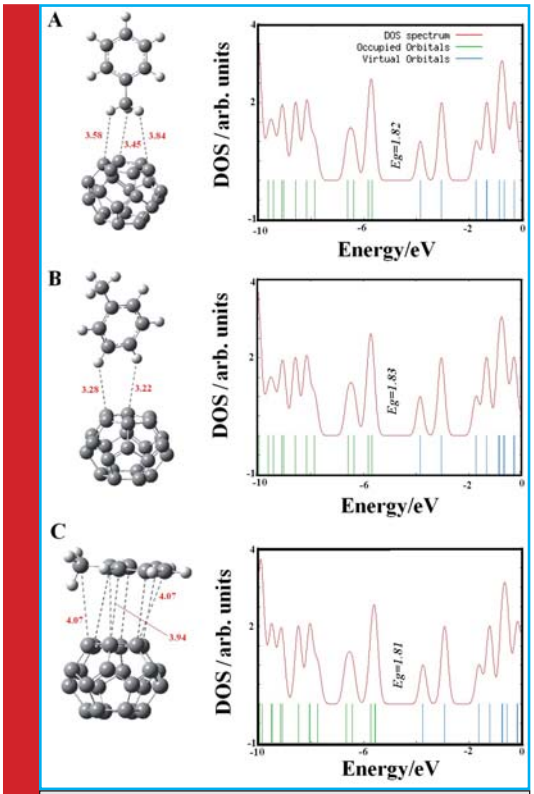

FIGURE 2. Different models of toluene adsorption on the C_{24} fullerene and their density of states (DOS). Distances are in Å.

close to the results of Liang Xu et al (2012) and Kumar et al (2011) respectively. Change of E_g of the Si-doped C_{24} fullerene is about 10.44% with respect to the pristine model, suggesting that the electronic properties of C_{24} fullerene is not very sensitive on the Si adsorption.

TOLUENE ADSORPTION ON THE C_{24}, SI-DOPED C_{24}, AND C_{20} FULLERENES

First, we computed the optimized structures of the individual toluene molecule and C24, Si-doped C24, and C20 fullerenes. Then, for investigation of toluene adsorption on the out surface of the fullerenes, several possible initial adsorption geometries including the parallel and perpendicular orientations of toluene molecule close to the surface of the fullerenes are considered. After full structural optimization without any constraints, the three most stable structures are obtained upon the relaxation processes for toluene adsorption on the C_{24} fullerene which are shown in Figs. 2 and their electronic properties are shown in Table 1.

In Configurations A and B in Fig. 2, the hydrogen atoms of toluene is interacted perpendicular to 5 and 6-membered rings of the C atoms of the fullerene with the minimum distance of about 3.45 to 3.22 Å, respectively. Calculated E_{ad} values of the configurations are about -1.80 and -3.22 kJ/mol, respectively and a maximum NBO charge of 0.01|e| is transferred from the fullerene to the toluene. The structural parameters of the configurations upon the adsorption process remain unchanged. The results show that the Configurations have a weak interaction between toluene molecule and the C_{24} fullerene. Also, in the configurations, the influence of toluene adsorption on the electronic properties of the fullerene was investigated and almost remains unchanged. HOMO and LUMO energies, energy gap (E_g), Fermi level energy (E_{FL}), and work function (Φ) of the configurations are shown in Table 1.

The E_{FL} in a molecule is approximately middle of E_g and Φ for a semiconductor is defined as the energy difference between the E_{FL} and the LUMO [24] which is important in field emission applications. The important sensing mechanisms in nanostructure devices is change of E_g the nanostructure and subsequently change of its conductivity upon the adsorption process as per Zhou et al (2010). Therefore, it is very important to calculate the DOS of the C_{24} fullerene in the configurations before and after toluene adsorption. DOS for the configurations is shown in Fig. 2. In comparison with the pure model,

Table 1: Adsorption energy (Ead) of toluene on C_{24}, Si-doped C_{24}, and C_{20} fullerenes, HOMO energies (EHOMO), LUMO energies (ELUMO), HOMO–LUMO energy gap (Eg), Fermi level energy (EFL), and work function (Φ) for the studied systems.

Structure	*Ead(kJ/mol)*	*EHOMO(eV)*	*ELUMO(eV)*	*Eg(eV)*	*aΔEg(%)*	*bQT|e|*	*EFL(eV)*	*Φ(eV)*	*cΔΦ%*
Toluene	-	-6.40	0.14	6.54	-	-	-3.13	3.27	-
C_{24}	-	-5.64	-3.82	1.82	-	-	-4.73	0.91	-
Fig. 2A	-1.80	-5.68	-3.86	1.82	0.00	-0.01	-4.77	0.91	0.00
Fig. 2B	-3.22	-5.68	-3.85	1.83	0.55	-0.01	-4.76	0.92	1.10
Fig. 2C	-3.18	-5.57	-3.76	1.81	0.55	0.00	-4.66	0.90	1.10
Si-doped C_{24}	-	-5.62	-3.99	1.63	-	-	-4.80	0.82	-
Fig. 3	-15.72	-4.38	-3.02	1.36	-16.53	-0.01	-3.70	0.68	17.04
C_{20}	-	-4.45	-3.71	0.74	-	-	-4.08	0.37	-
Fig. 4A	-6.26	-4.49	-3.76	0.73	0.72	0.00	-4.12	0.37	0.00
Fig. 4B	-60.16	-4.60	-3.18	1.41	91.21	0.17	-3.89	0.70	91.21

[a]The change of Eg of C_{24}, Si-doped C_{24}, and C20 fullerenes after toluene adsorption
[b]QT is defined as the total natural bond orbital charges on the toluene molecule (positive values show charge transfer from toluene molecule to the fullerenes)
[c]The change of work function of C_{24}, Si-doped C_{24}, and C_{20} fullerenes upon toluene adsorption

their E_g values remain almost unchanged (changed by about 0.55 %). Also, for the configurations, Fermi level energy (E_{FL}), and work function (Φ) values remain almost unchanged (changed by about 1.10 %). The results indicate that the toluene adsorption via these configurations has no sensible effects on the electronic properties of the fullerene.

In Configurations **C** in Fig. 2, the hydrogen atoms of toluene is interacted parallel to 5 and 6-membered rings of the C atoms of C_{24} fullerene with the minimum distances of about 3.94 Å. The E_{ad} value of the configuration is about -3.22 kJ/mol. In comparison with the pure C_{24} fullerene, its E_g, E_{FL}, and Φ values remain almost unchanged (see Table 1).

The above results show that C_{24} fullerene cannot be a potential efficient adsorbent or sensor for adsorption or determine of toluene from environments systems. Therefore, to solve this problem, introduced various functional groups and or the doping methods, which enables chemical covalent bonding between the fullerene and foreign atoms or molecules. Pure silicon can be doped with other elements to adjust its electrical response by controlling the number and charge of current carriers. Such control is necessary for transistors (Cui and Lieber (2001), solar cells, semiconductor detectors, and other semiconductor devices which are used in electronics and other high-tech applications.

Therefore, doping of C_{24} fullerene by Si atoms may be able to yield changes in the interactions between the fullerene and foreign atoms or molecules. Fig. 3 shows adsorption configuration of toluene molecule and its density of states (DOS) on the C_{24} fullerene doped with Si atom. The E_{ad} value of the configuration is about -15.72 kJ/mol, which is stronger than that in the pure C_{24} states. Nevertheless, the adsorption configuration is in the range of physisorption and cannot be used as potential efficient adsorbent for adsorption of toluene. For further study, the changes of E_g, E_{FL}, and Φ of the configuration is shown in Table 1. The values do not show notable changes. Therefore, the C_{24} fullerene doped with Si atom cannot be a potential efficient sensor for determine of toluene molecule. Also, Silicon doping cannot

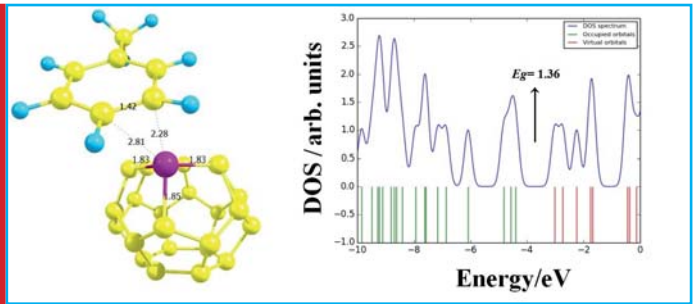

FIGURE 3. Toluene adsorption and its density of states (DOS) on the Si-doped C24 fullerene.

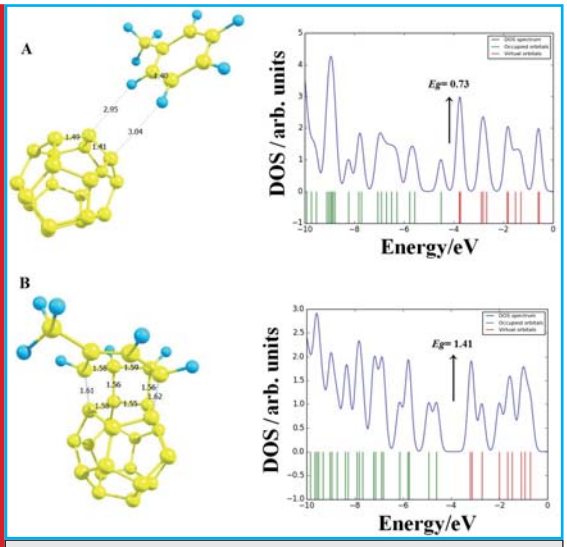

FIGURE 1. Adsorption configurations of toluene molecule on the C_{20} fullerene and their density of states (DOS).

significantly improve both the adsorption energy and electronic properties of C_{24} fullerene to toluene.

In the next step, the influence of the toluene adsorption on the electronic properties of the C_{20} fullerene was studied. After full structural optimization, the two most stable structures are obtained upon the relaxation processes which are shown in Fig. 4. In Configurations A and B in Fig. 4, the toluene is interacted perpendicular and parallel to surface of the fullerene. The E_{ad} value of toluene in Fig. 4A is -6.26 kJ/mol (a weak interaction) and in comparison with the pure C_{20} fullerene, its E_g, E_{FL}, and Φ values remain almost unchanged (see Table 1). The results showed that in this configuration, C_{20} fullerene cannot be a potential efficient adsorbent or sensor for adsorption or determine of toluene molecule. However, the E_{ad} value of toluene in Fig. 4B is -60.16 kJ/mol and also, the results show that the toluene adsorption through this configuration has sensible effects on the electronic properties of the fullerene. In this state, the E_g and Φ values are changed about 91.21% after the toluene adsorption. The important sensing mechanisms in nanostructure devices is change of E_g the nanostructure and subsequently change of its conductivity upon the adsorption process, (Zhou et al 2010). Therefore, the presence of the toluene molecule can be detected by computing the conductivity change of the C_{20} fullerene before and after the toluene adsorption. This behavior can be explained according to the following equation, (Li 2006).

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \qquad \text{Eq. (4)}$$

Where σ is the electric conductivity of the structure and k is the Boltzmann's constant. According to equation (4), smaller E_g at a special temperature leads to the larger electric conductivity. Therefore, the considerable change in E_g of the C_{20} fullerene shows the high sensitivity of electronic properties of C_{20}fullerene towards the toluene molecule. Also, it is well known that one of the most important factors in sensor devices is their recovery time (τ) that can be described as:

$$\tau = \nu_0^{-1} \exp\left(-E_{ad}/k_B T\right) \qquad \text{Eq. (5)}$$

Where k_B is the Boltzmann's constant, T is the temperature, and ν_0 is the attempt frequency. According to equation (5), more negative E_{ad} will prevent the recovery of the device. In other words, very strong interactions are not favorable in sensor devices due to long recovery times (τ). However, the E_{ad} value of the configuration is -60.16 kJ/mol (Table 1) that is not too large to hinder the recovery of the fullerene. The results show the high sensitivity of the fullerene towards toluene molecule and can be used as toluene sensor.

CONCLUSION

We have investigated the toluene adsorption on C_{24}, Si-doped C_{24}, and C_{20} fullerenes using DFT calculations. The results show that toluene molecule presents a weak physical adsorption with the pure and Si-doped C_{24}fullerene and the fullerenes are not a suitable adsorbent for toluene molecule. In addition, the results suggest that the pure and Si-doped C_{24} fullerene has low sensitivity to the presence of toluene and the influence of toluene adsorption on the electronic properties of the fullerenes remain almost unchanged. On the other hand, toluene molecule exhibits a high sensitivity upon C_{20} fullerene, so that the energy gap of the fullerene is changed about 91.21% after the adsorption process. The results show the high sensitivity of C_{20} fullerene towards toluene molecule and therefore can potentially be used for toluene sensors.

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