

Utility of extrinsic [60] fullerenes as work function type sensors for amphetamine drug detection: DFT studies

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ABSTRACT

Detection of illicit drugs is of increasing interest for police and drug communities because of their abuse. Using density functional calculations, we investigated the interaction of amphetamine (AA) drug with the pristine, B, Al, Ga (group IIIA), Si, and Ge (IIV group) doped C₆₀ fullerenes. The AA cycloaddition from its phenyl ring to the [6–6] bonds of C₆₀ is more favorable than that to the [5–6] bonds, in good agreement with experiment. When an AA molecule is adsorbed from its –NH₂ group on the C₆₀ fullerene, its work function is significantly decreased, showing a good sensitivity but the adsorption energy (–0.4 kcal/mol) is very small. Replacing a carbon atom of C₆₀ by the impurity atoms, the interaction between the AA and the C₆₀ is largely improved (adsorption energy ~ –38.6 to –65.6 kcal/mol). Upon the adsorption of AA on the doped fullerenes, the Fermi level is largely shifted to higher energy, especially in the case of Si and Ge-doped fullerenes, and thus, the work function decreases by about 22.7 and 24.9%, respectively. The electron emission largely increases which can be converted to an electronic noise. However, the Si and Ge-C₆₀ fullerenes are work function-type sensors for AA drug.

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1. Introduction

Detection of illicit drugs is of increasing interest because of the dramatic consequences of their abuse [1]. Amphetamine (AA) are popular drugs of abuse and their detection in the biological specimens is of great importance for police and drug communities [2]. It has been demonstrated, in the cases of abuse, several problems such as psychological disorders, and traffic accidents may occur [3]. Thus, developing highly sensitive, fast response, hand-portability sensors for detection of this drug agents is an essential task. Up to date, several detection methods have been introduced including infra-red absorption spectroscopy, gas chromatography, field asymmetric ion mobility spectrometry, etc [4,5]. By advent of nanotechnology, nanostructures have found widespread applications as chemical sensors because of their surface/volume ratio which is much greater than that of the conventional micro

detectors [6–16]. This character makes the large adsorption area available for adsorption process. Carbon nanotubes (CNTs), graphene and fullerenes are popular nanomaterials which have been investigated as gas sensors extensively [17–28].

It has been experimentally indicated that modification of fullerene surface by inserting impurity atoms is a promising method to improve its sensitivity to gas molecules [29]. This strategy also has been frequently employed for increasing the sensitivity of different nanostructures to chemicals [29–34]. Also, the interaction of C₆₀ fullerenes and its derivatives with different drugs has been extensively studied because of the potential application of C₆₀ in drug delivery [35–38]. Besides, expensive experimental methods, the computational approaches effectively help to understand the mechanism and the nature of these interactions [39–43]. It has been revealed that replacing a carbon atom of C₆₀ by Al or Si atom is a useful strategy to improve the drug delivery properties [44]. Also, experimentally many kinds of impurity doped C₆₀ fullerenes have been reported [45,46]. Nishinaga et al. have synthesized Al-doped C₆₀ fullerenes, growing on quartz glass and GaAs substrates by solid source molecular beam epitaxy [47]. Herein, we investigate the reactivity and electronic sensitivity of the intrinsic and extrinsic M-doped C₆₀ fullerenes M–C₆₀, M = B,

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Al, Ga (from group IIIA), Si, and Ge (from group IVA) to AA molecule, using density functional theory calculations.

2. Computational details

2.1. Methods

The all calculations were performed using the B3LYP functional with an empirical dispersion term (B3LYP-D) and the 3-21G* basis set as executed in the GAMESS code [48]. It has been already exposed that extending the basis set does not guarantee the improvement of the electronic properties compared to the experimental results, and 3-21G* results of the electronic properties are in good agreement with the experimental results [49,50]. Similarly, it gives dependable structures according to the different reports [51]. Also, to prove the reliability of the used basis set, we repeated some calculations with larger 6-31G* and 6-311++G** basis sets and compared the results. We set the self-consistence field (SCF) convergence criterion to 10^{-8} . Also, for the optimization, the maximum remaining force on an atom in the system as well as the average root mean square (RMS) force on all atoms thresholds are set to be about 4.5×10^{-4} and 3.0×10^{-4} , respectively. The maximum displacement, that is, the maximum structural change of one coordinate as well as the average (RMS) change over all structural parameters thresholds are set to be 1.8×10^{-4} and 1.2×10^{-4} , respectively.

The B3LYP is the commonest functional in the nanostructure examination, reproducing experimental data [52–60]. GaussSum code was used to attain DOS plots [61]. The adsorption energy (E_{ad}) is calculated as follows:

$$E_{ad} = E(\text{adsorbent}) + E(\text{AA}) - E(\text{AA/adsorbent}) + E(\text{BSSE}) \quad (1)$$

where $E(\text{adsorbent})$ is the total energy of an intrinsic or extrinsic C_{60} molecule. $E(\text{agent/adsorbent})$ is the total energy of the adsorbed AA molecule on the adsorbent surface. $E(\text{BSSE})$ is the basis set superposition error (BSSE) corrected for all adsorption energies using the counter poise method [62]. The nucleus independent chemical shift (NICS) values which were calculated using gauge independent atomic orbital (GIAO) approach [63]. The NICS is a descriptor of local aromaticity which has been introduced by Schleyer et al. [64]. For calculation of NICS(0) value, a ghost atom is located at the center of a definite ring and then an NMR calculation is performed. The NICS(0) parameter is then the opposite sign of shielding for the ghost atom.

2.2. Theory

The main purpose of this manuscript is predicting the sensitivity of work function (Φ) of the C_{60} and its impurity doped forms to the presence of AA drug. Experimentally, the Φ -type gas sensors work based on the Kelvin method which uses a Kelvin oscillator tool for calculating the Φ of a sample after and before the adsorption of gas molecules [65]. Applying this method, the change in the Φ ($\Delta\Phi$) due to the interaction of the sensor material with surrounding gas can be dignified. Sometimes, the concentration (or pressure) of a gas can be calculated by the amount of the $\Delta\Phi$ [66]. If the adsorbed gas molecules be able to change the Φ of the sensing material, it can affect the gate voltage, producing an electrical noise which helps the recognition of gases [67]. This method has been frequently used to detect gas molecules because it is very simple, but accurate, fast, and versatile and can be employed in many environments [68–71].

The Φ is the minimum energy needed (Fig. 1) to extract one electron to an infinite distance from the Fermi level of a material

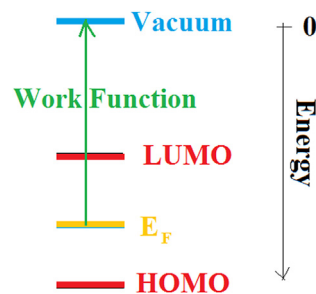


Fig. 1. A schematic view of Femi level energy, work function, and HOMO and LUMO levels of a semiconductor. The energy in vacuum is assumed to be zero.

$$\Phi = V_{el(+\infty)} - E_F \quad (2)$$

where $V_{el(+\infty)}$ is the electrostatic potential energy of the electron far from the surface which has been supposed to be zero, and E_F is Fermi level energy. Assuming $V_{el(+\infty)} = 0$, based on Eq. (2), $\Phi = -E_F$. As a usual way, the Fermi level energy is calculated as:

$$E_F = E_{HOMO} + (E_{LUMO} - E_{HOMO})/2 \quad (3)$$

where E_{HOMO} , and E_{LUMO} are the energies of HOMO and LUMO levels, respectively. The change of Fermi level, thereby, the Φ variation in a semiconductor alters the field emission properties because the electron current densities from a surface is exponentially related to negative value of Φ based on the classical Richardson Dushman equation [72,73]:

3. Results and discussion

3.1. The amphetamine molecule characterizations

Geometry of amphetamine ($C_9H_{13}N$) molecule and its molecular electrostatic potential (MEP) plot, HOMO, and LUMO profiles are shown in Fig. 2. The MEP plot displays that the N atom of amine group ($-NH_2$) has the highest negative electrostatic potential, and thus, the highest tendency to the electrophilic agents. Also, the carbon atoms has slightly negative electrostatic potential and the hydrogens are positively charged. The HOMO is approximately located on the amine group of the molecule and the LUMO is largely located on the phenyl group. The C–C bonds of phenyl group can be distinguished in three categories which are named as **1**, **2** and **3** in Fig. 2. The length of these bonds is approximately about 1.39 Å. The NICS(0) value in the center of hexagonal group is about -8.77 ppm, indicating a high aromatic character.

3.2. The AA adsorption on the pristine C_{60}

The pristine C_{60} fullerene has 90 C–C bonds which can be divided into [5–6] or [6–6] bonds which are shared between pentagon and hexagon or between 2 hexagons, respectively. The [6–6] bonds are smaller (~ 1.39 Å) and have more double bond character, compared to the [5–6] bonds (1.45 Å). The experimental values for these bonds are 1.40 and 1.45 Å, respectively [74]. 20 hexagon and 12 tetragons there exist in the structure of C_{60} . Two mechanisms can be expected for the interaction between the AA and C_{60} fullerene, including a cycloaddition from hexagonal ring of AA to a [6–6] or [5–6] bond of C_{60} , and adsorption from $-H$ atoms or N atom of $-NH_2$ group on the C_{60} .

3.2.1. Cycloaddition

Herein, we investigate the cycloaddition of AA molecule to the

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