Journal of Research in Pharmacy

Research Article

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Dopamine detection by doped single-walled carbon nanotube biosensors: A theoretical study

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Received: 29 December 2018 / Revised: 13 April 2019 / Accepted: 14 April 2019

ABSTRACT: In this paper, biosensors of the Fe-Nitrogen-doped zigzag (8, 0) carbon nanotube and Fe-doped zigzag (8, 0) carbon nanotube were offered for detection of dopamine molecule. The adsorption property and sensing mechanism of Fe-doped zigzag (8, 0) carbon nanotube and Fe-N-SWCNT (8, 0) with dopamine were investigated based on density functional theory. The obtained results demonstrated that both Fe-SWCNT and the Fe-N-SWCNT had good adsorption for dopamine, also conductivity also grew when they interacted with it. When dopamine is adsorbed on the surface of the single wall carbon nanotube, a large number of electrons transfer from the Fe-N-doped zigzag (8, 0) single carbon nanotube to dopamine, resulting in lessened frontier orbital energy gap and increased electrical conductivity. On the other hand, when dopamine is adsorbed on the surface of the SWCNT, the electrons transfer from dopamine to the Fe-N-SWCNT, the frontier orbital energy gap rises, while the electrical conductivity declines. Thus, Fe-nitrogen- SWCNT (8, 0) is more suitable and sufficient than Fe-SWCNT (8, 0) for dopamine detection.

KEYWORDS: Doped-single wall carbon nanotube (SWCNT); dopamine; density functional theory (DFT); interaction.

1. INTRODUCTION

Given their excellent sensing behaviors including fast response, low priced, good sensitivity, and being environmentally friendly, carbon nanotubes (CNTs) have been engrossed a great deal of attention as a new member of sensors and a novel sensing material applied for gas sensing and detection [1]. As well as, CNTs have a large potential to mediate fast electron-transfer kinetics for a wide range of electroactive species such as hydrogen peroxide, owing to high surface-to-volume ratio [2]. It has been presented that the electronic properties of CNTs can be moderated by vacancy defects electronic field [3, 4] filling some species inside the CNTs [5], in addition physical or chemical adsorptions on the side wall of the tubes [5]. On the other hand, non-covalent modification of CNTs has been developed for different uses such as drug delivery, biochemical sensors, gene delivery, and therapeutic applications [6]. An appropriate technique to supply single-walled carbon nanotubes (SWCNTs) to detect gas molecules especially organic chemicals and biological substances is doping with heteroatom substitution. The adsorption sufficiency of SWCNTs can be amender through introducing heteroatom impurities (such as silicon, boron, zinc, titanium and nitrogen) and creating active sites in tube walls [7].

Further, doped CNT sensors can raise their adsorptivity, therewith modifying their sensing property towards gases, due to the strong electron accepting/withdrawing behavior of transition metals [8]. Investigations [9] have suggested that transition metals have a wealthy d-electron and empty orbital, to which the tiny gas molecule can bond strongly when adsorbed on the surface. Newly, carbon nanotube-based sensors have been applied for the detection of biomolecules and other bio-related applications [10]. Dopamine (DA) as one of the most momentous catecholamine neurotransmitters [11], could be involved in many neurological mechanisms, from the extrapyramidal motor tracts of the central nervous system to psychostimulants' addiction [12]. As such, as well as to the relevance of detecting it accurately, also been used as a potent drug for activating receptors in the brain, heart muscle, kidney, and gut [13]. Additionally, it has an important role in detecting emergence of Parkinson's disease, drug abuse, and HIV infection of some cells [14-16]. Necessity of exact and correct detection at physiological levels of dopamine, is the principal factor for the progress of several techniques including electrochemistry [17], chromatography [18], gravimetric [19], and optical

How to cite this article: Madadi Mahani N. Dopamine detection by doped single-walled carbon nanotube biosensors: A theoretical study. J Res Pharm. 2019; 23(5): 785-791.

https://doi.org/10.35333/jrp.2019.25

ISSN: 2630-6344

spectroscopy [20]. At physiological levels, the dominant presence of ionized DA has been reported from both experimental [21] and theoretical [22] results.

Carbon nanospikes (CNS) on several types of metal wires to develop an electrochemical sensor for dopamine detection have investigated by Alexander et al. [23]. Sansuc et al. have developed ultrasensitive detection of dopamine using a CNT network microfluidic flow electrode [24]. A graphene-modified acupuncture needle for dopamine detection has introduced by Tang et al. [25]. The efficiency of a SWCNT modified gold electrode for dopamine sensing by cyclic voltammetry have been studied by Kurniawan et al. [26]. Also, they investigated interfering effect of biological molecules like ascorbic acid (AA) in determining dopamine and have not observed anyinterference signal from ascorbic acid (AA) during DA etection. Ab initio first principles methods have been used to probe the adsorption mechanism of NO_2 gas on M-doped (Ti, Cu, and Pt) SWCNT (8,0) to determine the most efficient combination for NO_2 sensing [27]. A density functional theory (DFT) study has been performed on Rh-doped CNT biosensors for prediagnosis of lung cancer and detection of CO_2, C_6H_6 and C_6H_7N gases [28]. Also, another DFT study has been performed on a new novel bionanosensor hybrid of tryptophan/Pd doped single walled carbon nanotube [29].

Density functional theory calculations by Yeh et al. has performed for study of adsorption of dopamine on semiconducting (6, 5) SWNT, including pure, and B, N co-doped (6, 5) SWNTs [30]. Their results have indicated that DA can form multiple molecular interactions with pure (6, 5) SWNT. SWCNTs have been modified using Fe and nitrogen to improve their intrinsic characteristics, where this modification has become a research hotspot. The DFT calculation-based method GGA has been conducted to study the interaction of dopamine and nitrogen-Fe doped single carbon nanotube (8, 0).

2. RESULTS AND DISCUSSION

The Fukui indices enable for identifying the reactive regions as well as the electrophilic and nucleophilic behavior of a molecule along with its chemical reactivity. For a limited system, when a molecule is accepting electrons, it has the Fukui index for nucleophilic attack (f^+), while when the molecule is donating electrons, it has the Fukui index for electrophilic attack (f^-). Accordingly, HOMO and LUMO are related to negative and positive Fukui indices, respectively:

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{v(r)} = \rho(r)_{N+1} - \rho(r)_N = |\varphi_{LUMO}(r)|^2 = \rho_{LUMO}(r) \quad \text{(Eq. 1)}$$

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{v(r)} = \rho(r)_N - \rho(r)_{N-1} = |\varphi_{HOMO}(r)|^2 = \rho_{HOMO}(r) \quad \text{(Eq. 2)}$$

The Fukui indices permit forecasting where the most electrophilic and nucleophilic sites of the drug molecule are. Fukui indices calculations as well as DFT-based reactivity descriptor were used in the characterization of the preferred reactive sites, thereby providing a firm explanation for the reactivity of the dopamine molecule.

The Fukui indices for the dopamine molecule in the gas phase are presented in Figure 1. In this figure, the O(0.121) atom represents the nucleophilic sites of the molecule. This figure shows that the Fukui indices (f^-) are scattered throughout almost the entire molecule. The N1 (0.135) and C2 (0.124) atoms have the highest nucleophilic electron density and the highest electrophilic electron density.

The Fukui indices for the dopamine molecule in the solution phase almost similar to Fukui indices in the gas phase. After geometric optimization, the obtained model of Fe-CNT and dopamine molecule was incorporated into the same space to precede the adsorption processes, i.e. initiating the integral optimization of the whole system, with the final relaxed configurations displayed in Figure 2(b). The adsorption energy of dopamine and Fe-SWCNT has been -3.2141 eV, whereas the adsorption energy of dopamine and Fe-N-SWCNT (8, 0) has been obtained as -3.6286 eV. İn solution phase, the adsorption energy of dopamine and Fe-SWCNT has been gained -3.2652 eV, whereas the adsorption energy of dopamine and Fe-N-SWCNT (8, 0) has been gained as -3.7362eV.

These data display that the adsorptions are exothermic and spontaneous. The negative values of adsorption energies indicate the strong interaction in these systems; the more negative these values are, the more easily the process would occur. More specifically, such interactions can be conceived as chemisorption due to the large *E*ad. The energy gap (E_g) of Fe-CNT/DA system decreased to 0.096 eV from 0.099 eV for pure Fe-CNT system as presented in Table 1, suggesting the growing conductivity for Fe-CNT after dopamine adsorption.

Table 1. E_{HOMO}, E_{LUMO} and E_g * of different systems.

System	E_{HOMO}(eV)		E_{LUMO}(eV)		E_g(eV)*	
	Gas phase	Solution phase	Gas phase	Solution phase	Gas phase	Solution phase
Fe-SWCNT	-3.792	-3.961	-3.693	-4.001	0.099	0.102
N-Fe-SWCNT	-3.654	-4.089	-3.561	-3.956	0.093	0.088
Fe-SWCNT-DA	-3.608	-4.047	-3.512	-3.995	0.096	0.091
(N-Fe-SWCNT)-DA	-3.791	-4.081	-3.707	-4.001	0.084	0.086

*Eg = E_{LUMO} −E_{HOMO}

Also, in solution phase, energy gap (E_g) of Fe-CNT/DA system decreased from 0.102 to 0.091 for pure Fe-CNT system.

The density distributions of HOMO and LUMO changed to -3.608eV for E_{HOMO} and -3.512eV for E_{LUMO}. With regard to Table 1, the energy gap (E_g) of Fe-N-SWCNT (8, 0)/DA system decreased to 0.084 eV from 0.093 eV for pure Fe-N-SWCNT system, revealing the enhancing conductivity for Fe-N-SWCNT after dopamine adsorption. Also, İn solution phase, energy gap (E_g) of Fe-CNT/DA system decreased from 0.088 to 0.086 for pure Fe-CNT system.

Also, the density distributions of HOMO and LUMO changed to -3.791eV for E_{HOMO} and -3.707eV for E_{LUMO}.

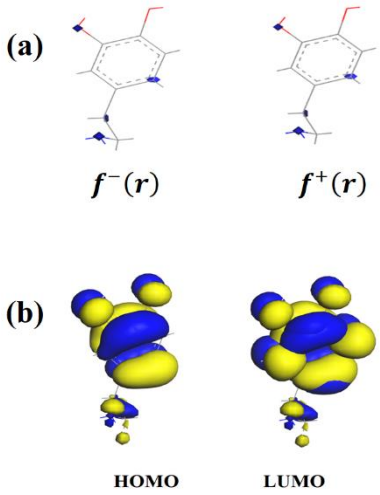

Figure 1. Fukui indices, HOMO and LUMO distributions of dopamine.

Note that after adsorption, the density of HOMO and LUMO distribution has transformed particularly those areas near the Fe and N atoms, with the underlying assumption that strong electronic transfer occurred surrounding the Fe and N dopants. The Fe and N atoms can provide some activated sites for the dopamine molecule adsorption causing density redistribution of the two orbitals thereby leading to conductivity alteration of Fe-N-SWCNT after the adsorption process. The orbital distributions of each system are shown in Figure 2. Figure 3 demonstrates that the LUMO is almost distributed throughout the molecule 1, while the HOMO is distributed across the molecule.

Also, the HOMO and LUMO move toward the nucleus whereby the orbital energy drops. Fe-SWCNT and Fe-SWCNT are a p-type semiconductor. The transferred electrons increase the number of electron holes and simultaneously raise the number of carriers, enhance the conductivity, and reduce the frontier orbital energy gap. The presence of an iron and nitrogen atoms would create the suitable spaces on the nanotube for the adsorption between dopamine and carbon nanotubes. The results both gas and solution phases, revealed that the adsorption of dopamine on the outer surface of carbon nanotubes was energetically favorable and the reactivity of Fe-N- doped complexes increased compared to pristine carbon nanotubes.

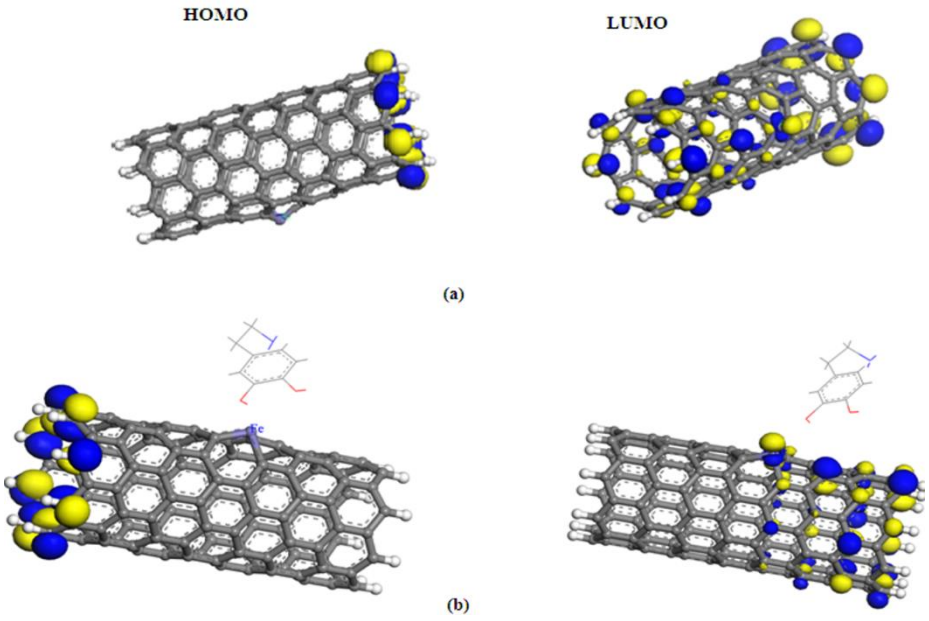

Figure 2. HOMO and LUMO distributions of Fe-CNT (**a**) and Fe-CNT-DA (**b**).

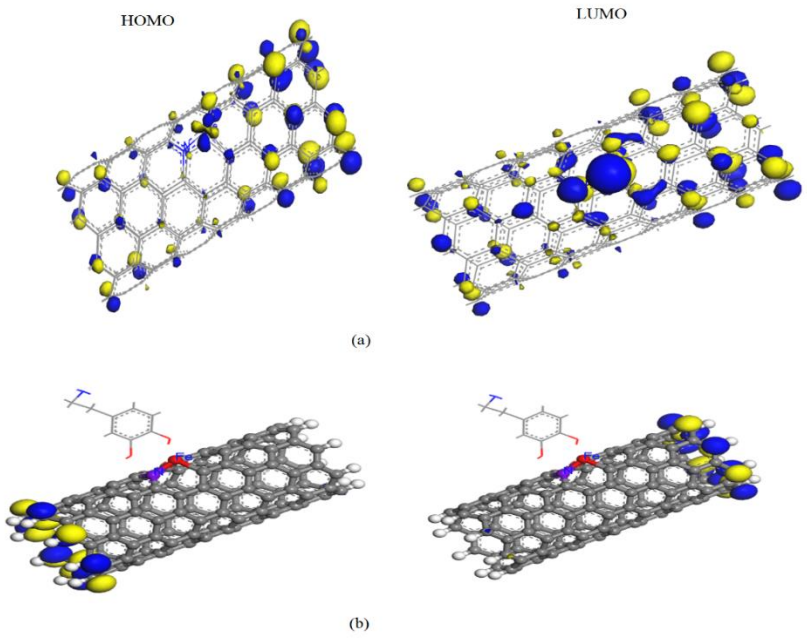

Figure 3. HOMO and LUMO distributions of Fe-N-SWCNT (**a**) and Fe-N-SWCNT-DA (**b**).

3. CONCLUSION

This work simulated the adsorption behaviors of Fe-SWCNT and Fe-N-SWCNT (8, 0) upon dopamine molecule addition to detect dopamine with DFT approach. Also, the sensitivity of the Fe-SWCNT and Fe-N-SWCNT to dopamine was investigated. The interactions between the Fe-SWCNT and Fe-N-SWCNT and dopamine were exothermic; however, the adsorption energy of Fe-N-SWCNT was more satisfactory. Further, the frontier orbital energy gap diminished. The theoretical calculation results inferred that Fe-N-SWCNT can have good sensitivity to the dopamine molecule. Thus, both Fe- SWCNT and Fe-N-SWCNT (8, 0) can be suitable options for dopamine molecule detection. These results are helpful in the development of CNT-based sensors and provides a theoretical basis for developing Fe-N-SWCNT-based sensors; the outcomes also

indicated that the Fe- and N-doped adsorbents had a superior sensing property. The aim of this study was to suggest desirable sensing materials for future application as biosensors in the field of disease diagnosis and detection of drugs.

4. MATERIALS AND METHODS

All calculations were performed using DMol^3 code [31] which is based on DFT. Consequently, the electronic wave functions were extended in numerical atomic basis sets explained an atomic-centered spherical polar mesh. The electron density in DMol^3 was extended in terms of atomic-centered partial densities with multipolarity capable of carrying out both all-electron or pseudo-potential calculations. The double numerical plus d-function all electron basis set was employed for calculations. The DND basis set involves one numerical function for each occupied atomic orbital and a second set of functions for valance atomic orbitals, plus a polarization d-function on all atoms. This basis set is comparable with the Gaussian 6-31G*. The excellent modality of these basis sets minimizes basis set superposition effects and authorized better explanation of molecular polarizabilities. The density function is treated within the generalized gradient approximation with exchange correlation potential demonstrated by Wang and Perdew method (GGA-PW91) [32].

Conductor-like Screening Model (COSMO) as implemented in DMol^3 [33] has been chosen for calculation in solution phase, which allow for the treatment of solvation effects. The deviations of this COSMO approximation from the exact solution are small. Firstly, the (8 0) SWCNT was selected as the pristine model of the SWCNT, based on which Fe-SWCNT and N-Fe-SWCNT were developed. When Fe is doped on the perfect surface of a pristine nanotube and a nitrogen-single nanotube or away from the surface defects, the interaction between the Fe and the nanotube is weak.

Further, this is difficult that constructing a stable structure for adsorption. When Fe is adsorbed on the point defect site of the nanotube surface, the structure becomes stable. Initially, the Fe-SWCNT model was built in this stable structure, with the geometry optimization structure demonstrated in Figure 2(a). The radius of the Fe atom is remarkably greater than that of the C atom; thus, the Fe atom of a Fe-SWCNT is highlighted on the nanotube surface. The bond lengths between the Fe atom and the three neighbor C atoms are 0.14178 (Fe –C1), 0.14172 (Fe –C2), and 0.14173 nm (Fe –C3).

The adsorption energy (E_{ads}) between the dopamine molecule and nanotube can be obtained using the following formula:

$$E_{ads} = E_{System} - E_{\mathrm{Fe-SWCNT}} - E_{dopamine} \quad \text{(Eq. 3)}$$

Where, E_{ads} represents the total energy of the adsorption structure, $E_{\mathrm{Fe-SWCNT}}$T is the energy of Fe-SWCNT, and $E_{dopamine}$ is the energy of one isolated dopamine molecule.

In the same vein, the Fe-Nitrogen SWCNT model was built in this stable structure, with the geometry optimization structure displayed in Figure 3(a). The radii of the Fe atom and nitrogen atom are remarkably greater than that of the C atom; thus, Fe and N atoms in Fe-N -SWCNT are highlighted on the nanotube surface.

The adsorption energy (E_{ads}) between the dopamine molecule and the nanotube can be calculated using the following formula:

$$E_{ads} = E_{System} - E_{\mathrm{Fe-N-SWCNT}} - E_{dopamine} \quad \text{(Eq. 4)}$$

Where, E_{ads} represents the total energy of the adsorption structure, $E_{\mathrm{Fe-N-SWCNT}}$ shows the energy of Fe-N-SWCNT, and $E_{dopamine}$ denotes the energy of one isolated dopamine molecule. All values of energies are obtained by optimization of the geometry structure. In addition to energy, we also calculated the electronic properties obtained from the local and net charge transfers as well as the electron density according to the Milliken charge population.

Acknowledgements: I gratefully thank Payame Noor University for financial support. The authors would like to express their appreciations to department of chemistry this university for providing research facilities.

Author contributions: Concept – N.M.M.; Design – N.M.M.; Supervision – N.M.M.; Materials – N.M.M.; Data Collection and/or Processing – N.M.M.; Analysis and/or Interpretation – N.M.M.; Literature Search – N.M.M.; Writing – N.M.M.; Critical Reviews – N.M.M.

Conflict of interest statement: The author declared no conflict of interest.

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