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Solvent effects on the stability and the electronic properties of histidine/Pd-doped single-walled carbon nanotube biosensor

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ABSTRACT

The nanobiosensors physical and chemical properties are affected by the nature and the interactions with the solvent molecules. To develop a new biosensing concept for the detection of biological agents in both in vivo and in vitro, identifying the non-specific influence of the solvent on the chemical reactivity and the stability of the nanobiosensors is crucial. In this paper, the self-consistent reaction field theory (SCRF) was used to investigate the solvent effects on the structure and electronic properties of the hybride of Pd doped single-walled carbon nanotube (Pd/SWCNT) and histidine amino acid as a new generation of nanobiosensors. These effects will be investigated in three polar mediums using density functional theory (DFT) calculations in the combination with the polarizable continuum model (PCM). The emphasis will be on the results of the Quantum Theory Atoms in Molecule (QTAIM), Natural bond orbital (NBO) and the Frontier Molecular Orbital (FMO) analysis. The conceptual DFT based reactivity and stability descriptors, chemical potential, hardness and electrophilicity index were calculated in different solvents in ground state to study how the structure and electronic properties will be affected by solvents. Molecular electrostatic potential map was performed by DFT method. The value of the electrostatic potential is largely responsible for the binding of a substrate to active sites of biosensor. The presence of heterocyclic organic compound and electronegative atoms in the biological receptor of the His/Pd/SWCNT nanobiosensor will result in strong solvent-solute interactions. With increasing the electric permittivity of solvents, the stabilization energies of various conformations of nanobiosensor shifts to lower value because of the additional attractive interactions between the nanobiosensor and the solvent. The His/Pd/SWCNT presents high stability with considerable values of stabilization energies, charge transfer and sensible energy bond gap in polar medium which confirm both in vitro and in vivo biosensing application.

1. Introduction

Since 2000 with the first use of carbon nanotube (CNT) as sensor by Kong et al. [1], individual nanotubes have been demonstrated to be promising molecular platform in sensing application due to their fast response time and high sensitivity at room temperature. The excellent structural and electrical properties of CNTs have stimulated great focus on the application of these nanomaterials as physical transducers in biosensors [2].

Higher performance in sensitivity and selectivity will be offered by biosensors rather than other diagnostic devices. L.L. Clark in Cincinnati USA, developed the biosensors to measure the dissolve oxygen in blood [3]. Biosensors comprise of a biological entity as sensing element combined with a physicochemical detector component. Nanobiosensors are widely used due to their promising applications in clinical and diagnostic analysis, detection and monitoring of biological processes, industrial processing and monitoring and environmental pollution monitoring [3–9]. The outstanding ability to fast electron transfer kinetics, compatible size with the biological structures and low detection limits of single walled carbon nanotubes (SWCNTs) are the great characteristics in the fabrication of SWCNT-based biosensors. SWCNT, a cylindrical nanostructure with high aspect ratio, and the greater area of contact, formed by rolling up a single graphite sheet into a tube, can enhance the chemical reactivity of biomolecules [10–12]. Because of the week van der Waals interaction of smooth surface of nanotube nanotube surface with the adsorbents, the sensitivity and the selectivity of SWCNT towards a specific analyte could be improved by chemical functionalization. One of the most effective modification of the surface of SWCNTs and thus introducing additional electronic states in the Fermi levels and enhancement of their adsorption potential, is the doping, i.e. heteroatom substitution into the lattice of SWCNTs [13–16]. The biocompatibility and the stability of the SWCNT-based biosensors can improve the sensing behavior of these materials. Denis et al. had theoretically investigated the stability of SWCNT [17]. The noncovalent interaction of amino acids with the doped SWCNTs would change the

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Table 1
Adsorption energies (kcal mol^{-1}) and the dipole moment (D) of complexes in three solvent using PCM model.

	Water($\varepsilon = 78.39$)		DMSO($\varepsilon = 48.90$)		Ethanol($\varepsilon = 24.55$)	
Complex	Eads	Dipole moment	Eads	Dipole moment	Eads	Dipole moment
Amine Site	−15.435	17.8	−15.606	17.7	−15.968	17.4
Carbonyl site	−10.320	12.9	−10.551	12.8	−11.025	12.6
Imidazol ring site	−2.737	5.8	−2.742	5.7	−2.772	5.3

electrical conductance of SWCNT-based sensors by charge transfer between Pd/SWCNT and His adsorbed via the local chemical reactivity [18] and lead to efficient detection of a variety of biomolecules and further progress in biomedical applications. In our previous studies [14], we have designed a new type of modified nanobiosensors through doping impurity atom into SWCNT, the His/Pd/SWCNT.

The function of biologically active molecules depends on their structure and on the intermolecular interaction with the solvent which influence biological processes. In this study, an attempt has been made to explore the structural stability, adsorption energies, reactivity parameters and molecular orbital properties in three different polar solvent medium including, water, DMSO and ethanol and DMSO using PCM. In continuum models the solvent treated as a continuum, with a uniform dielectric constant surrounding a solute molecule which is placed in a cavity and immersed in a continuous medium. The polarization of the media induced by the solute electric field will react with the solute system.

Results have been compared to estimate the variation of electronic properties of investigated nanobiosensor. The study of solvent effects plays an important role in biocompatibility of these sensors, i.e. the ability of a sensor to perform with an appropriate host response in a specific application [19].

2. Computational details

Gaussian 03 program package [20] has been used to calculate geometry optimization and solvent effects. Density functional calculations with Beck's three parameter hybrid method (B3) [21] using correlation functional of Lee, Yang, Parr [22] (B3LYP) level have been performed. Different basis sets were tested and all geometry full optimization have been performed with hybrid density functional B3LYP/6-31G(d) and DGDZVP extra basis set for Pd atom as showed good ability in study of long range interactions. The absence of imaginary frequency at the same level verified the optimized structures correspond to the energy minima. Three solvent, water ($\varepsilon = 78.39$), DMSO ($\varepsilon = 48.9$) and ethanol ($\varepsilon = 24.55$) were selected to study the solvent effects on titled parameters using Tomasi's polarized continuum (PCM) model [23]. Adsorption energies in solvent were calculated according to Eq. 1.

$$E_{ads} = E_{His/Pd/SWCNT} - (E_{Pd/SWCNT} + E_{His}) \quad (1)$$

were $E_{His/Pd/SWCNT}$ is the total energy of Pd/SWCNT with histidine molecule and $E_{Pd/SWCNT}$ and E_{His} are the total energy of Pd/SWCNT and histidine molecule in relax geometry respectively. The noncovalent interaction of histidine (His) molecule with Pd/SWCNT were considered via different initial configuration complexes i.e. amine, carbonyl and imidazole ring sites through the perpendicular direction to SWCNT to reduce the unfavorable interactions.

The natural bond orbital (NBO) [24] was carried out to quantify the charge transfer between His and Pd/SWCNT at the same level. AIM 2000 package was employed to deep understanding of the nature of interactions in different solvent medium via the Bader's quantum theory of atom in molecules (QTAIM) [25].

Chemical reactivity and stability indexes were calculated as defined in Eqs. 2–5 according to Koopmans theorem [26]:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V(r),T} \quad (2)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{V(r),T} \quad (3)$$

$$S = 1/2\eta \quad (4)$$

$$\omega = \mu^2/2\eta \quad (5)$$

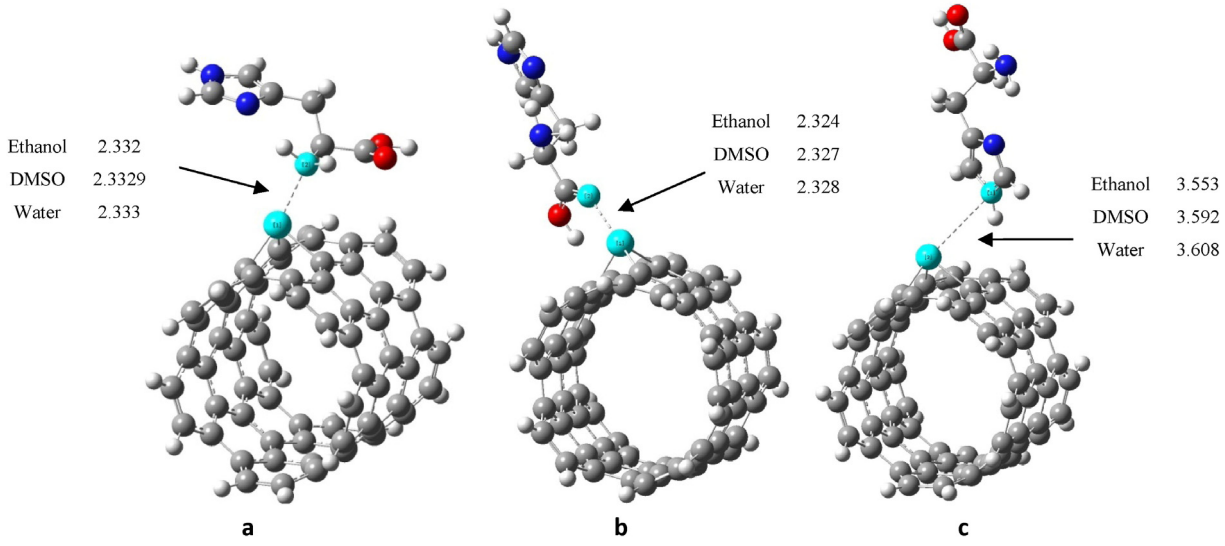

Fig. 1. Optimized geometries of His/Pd/SWCNT a. amine site b. carbonyl site and c. imidazol ring site adsorption with the interatomic distances in angstrom.

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