

A DENSITY FUNCTIONAL THEORY-BASED INVESTIGATION OF THE FUNCTIONALIZATION DENSITY DEPENDENCE OF THE SOLUBILITY OF SINGLE-WALLED CARBON NANOTUBES

Michael Mananghaya, Emmanuel Rodulfo, Gil Nonato Santos

Abstract—Chemical Functionalization is a technique used to increase the dispersion and solubility of single-walled carbon nanotube (SWCNT). Functionalization of a (10, 0) zigzag nanotube segment containing 80 C atoms was investigated with the aide of spin-unrestricted density functional theory (DFT). The (10, 0) was funtionalized with three organic acid groups: (a) carboxylic acid, (b) aromatic dicarboxylic acid, and (c) aromatic sulfonic acid. The functionalization was found out to be stable and bonding is favorable. Functionalization results in an enhancement in the solubility of the nanotubes in water. Further as the degree of sidewall functionalization increases, the SWCNT sample becomes more soluble. Binding energies, dipole moments and the Gibbs free energies of solvation were calculated.

Index Terms— Binding Energy, Density Functional Theory, Gibbs Free Energy of Solvation, Single-Walled Carbon Nanotubes.



1 INTRODUCTION

Single-walled carbon nanotubes (SWCNT) are allotropes of carbon possess unique mechanical, optical, and electronic properties; these properties are best realized when they are dispersed as individuals [1]. However, the heterogeneity in length, diameter, and chirality as well as the strong van der Waals forces of the as-produced SWCNT samples makes it difficult to obtain individualized SWCNTs that retain their intrinsic properties in applications specifically intended for nanomedicine [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11]. Because of this, it is imperative to examine the dispersion of SWCNTs as individuals in a liquid and hopefully address the toxicity of these carbon-based nanostructures [12], [13], [14], [15].

Carbon nanotubes (CNT) are generally insoluble in water. In this respect, the strong van der Waals interactions between SWCNT sidewalls have made dispersion in fluids very difficult. The dispersion problem has to be overcome in part by chemical functionalization of the CNT surface [7], [8], [9], [10], [17]. The dispersion of SWCNTs as individuals in a liquid has allowed for a better understanding of their spectroscopic properties,

thereby opening up research areas such as biosensing and targeted therapy for cancer treatment. Moreover, individual SWCNTs in solution are more accessible for chemical manipulation and cutting leading to improved compatibility with a variety of biological components [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15].

Essentially fundamental problems such as the need to improve solubility, as well as the need to diminish the toxicity of the CNT [1] are addressed in this paper through computational simulation and modeling with the aide of density functional theory (DFT) calculations [16] to investigate how the properties of water-dispersible SWCNTs functionalized with different doping concentrations of acid groups change in an effort to determine the solubility as a function of the degree of sidewall functionalization. Functionalization enhances the biocompatibility, the way to rational modifications and/or design of new nanostructures is proven to potentially diminish its toxicity, and therefore paving species for efficient drug delivery and diagnostic applications.

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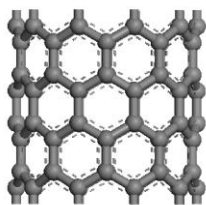


Fig.1. Optimized geometry of the infinite (10,0) zigzag SWCNT. Gray color depicts carbon atoms.

2 METHODOLOGY

A (10, 0) zigzag nanotube segment containing 80 C was used as a model to investigate the effects of functionalization of SWCNT in increasing the solubility of SWCNT, see side view in Fig. 1. Sidewall of the nanotubes were functionalized with the following organic acid molecules: (a) formic acid, CO_2H_2 , as a model of carboxylic acid, Fig. 2 [9], [10], (b) isophthalic acid, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, as a model aromatic dicarboxylic acid, see Fig. 3, [18] and (c) benzenesulfonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, as a model aromatic sulfonic acid, see Fig. 4, [18]. These organic acid molecules have been investigated in hope for design of species for efficient dispersion capability for drug delivery.

All calculations were performed using DFT with a PBE functional [19] and each electronic wave function is expanded in a localized atom-centered basis set with each basis function defined numerically on a dense radial grid. For supercell geometries, spin-unrestricted calculations were carried out with a double numeric polarized (DNP) basis set available and the atomic cutoff set as high as 4.60 Å. Charge densities were analyzed by the Mulliken method [20]. For open-shell molecular radicals, the unrestricted formalism was used. The present level of calculation, DFT (GGA-PBE)/ DNP, is known to produce reasonable results [21] for bond lengths, bond angles, and bond energies for a wide range of molecules. The computations were carried out on a computer using the ab initio quantum chemistry package, *Dmol³* code, available from Accelrys [22] with five Monkhorst-Pack k-points used for the Brillouin zone integration along the axes of (10, 0) nanotube. Geometry optimizations with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm were performed with convergence criterion of 0.005 Å on displacement, and 10^{-5} a.u. on the total energy and electron density. A hexagonal lattice was used to simulate the SWCNT, with a wall-to-wall distance of at least 10Å , sufficient to avoid in-plane interactions between nanotubes in adjacent unit cells.

Electronic structure descriptors have been computed to analyze the geometrical and electronic changes that may lead to better solubility of the functionalized nanotubes. Among them are the dipole moment (μ_{dip}) and the Gibbs free energy of solvation (ΔG_{soliv}). Measuring its Gibbs free energy of solvation can

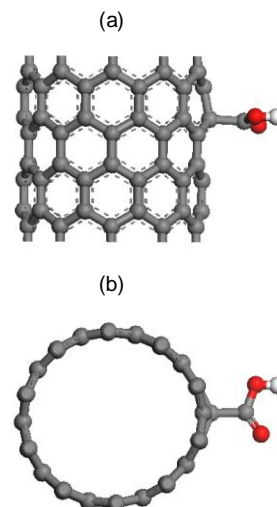


Fig.2. Optimized geometry of the infinite (10, 0) zigzag SWCNT with the formic acid radical at the tube sidewall. (a) Side view, (b) top view. Gray color depicts carbon atoms; white is hydrogen and red is oxygen

assess the solubility of a given molecule in a solvent. A number of quantum mechanical continuum solvation models were developed for this purpose [23], [24]. We have chosen the Conductor-like Screening MOdel (COSMO) as implemented in *Dmol³* [22]. These originated from the Onsager continuum model [24], and were formulated as continuum solvation model (CSM) by Tomasi et al. [23], [25], [26], [27]; *Dmol³* includes certain COSMO controls, which allow for the treatment of solvation effects. The solute molecule in COSMO continuum solvation model forms a cavity within the dielectric continuum of permittivity, ϵ that represents the solvent: The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric medium is described by the generation of screening (or polarization) charges on the cavity surface. In contrast to other implementations of CSMs, COSMO does not require solution of the rather complicated boundary conditions for a dielectric in order to obtain screening charges, but instead calculates the screening charges using a much simpler boundary condition for a conductor. These charges are then scaled by a factor to obtain a good approximation for the screening charges in a dielectric medium. The deviations of this COSMO approximation from the exact solution are small. For strong dielectrics like water, they are typically less than 1%

3 RESULTS AND DISCUSSIONS

3.1. Structure and electronic properties

We have used the *Dmol³* code to optimize the geometries for the finite SWCNT. The resulting optimized structures are shown in Fig. 1. The infinite (10, 0) nanotube has an optimized length of 12.78Å , and a diameter of 7.83Å . Computed length and diameter agrees with Mananghaya et al. [28]. Presented in Fig. 2 is the optimized structure for one possible way of functionalizing the infinite SWCNT with formic acid radical is shown in Fig. 2. The

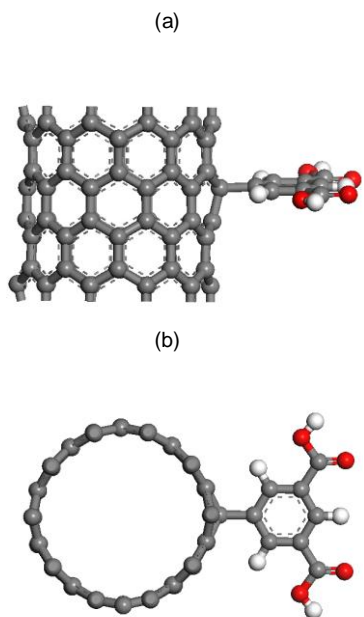


Fig.3. Optimized geometry of the infinite (10, 0) zigzag SWCNT with the isophthalic acid radical at the tube sidewall. (a) Side view, (b) top view. Gray color depicts carbon atoms; white is hydrogen, and red is oxygen.

functionalization is at the sidewall of the nanotube wherein we take the organic molecule already in its radical form, $\cdot\text{CO}_2\text{H}$, attached by its C atom to the nanotube sidewall [29]. The optimized structure for the functionalization of the SWCNT sidewall with the isophthalic acid radical $\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$ is given in Fig. 3. We have also studied the functionalization of the SWCNT sidewall with the benzenesulfonic acid radical, $\cdot\text{C}_6\text{H}_4\text{SO}_3\text{H}$, the optimized structure is shown in Fig. 4. These molecules have been used in studies of covalent functionalization of SWCNT capability for drug delivery [15, 18]. Since one of the objectives of the calculation is to investigate how the solubility of SWCNTs change as a function of the degree of sidewall functionalization, therefore the resulting optimized structures is presented in Fig. 5 as a model for determining the dependence of solubility with respect to the percentage of the added formic acid radical. The density of functionalization on the sidewalls of the SWCNT is reported as the percentage of the addends to SWCNT carbon atoms ($\#$ of acid group/ $\#$ of carbon) \times 100%. For the functionalization of the SWCNT sidewall with the isophthalic acid radical and benzenesulfonic acid radical we simply replace the configurations in Fig. 5 with the $\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$ and $\cdot\text{C}_6\text{H}_4\text{SO}_3\text{H}$ radicals respectively.

Binding energies of the radicals to the nanotube, E_b , are defined for the reaction



where ORG is any of the studied organic radicals and ORG-SWCNT is the corresponding functionalized nanotube. Therefore

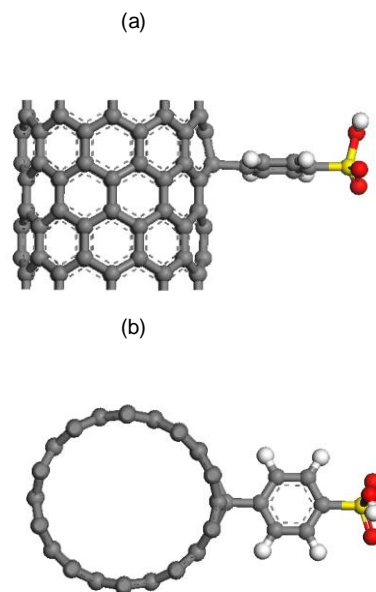


Fig.4. Optimized geometry of the finite (10, 0) zigzag SWCNT with the benzenesulfonic acid radical at the tube sidewall. (a) Side view, (b) top view. Gray color depicts carbon atoms; white is hydrogen, yellow is sulfur and red is oxygen.

$$E_b = E(\text{SWCNT}) + E(\text{ORG}) - E(\text{ORG-SWCNT}). \quad (2)$$

where E denotes the total energy of the optimized system in the bracket. If functionalization is thermodynamically favorable the binding energy is positive corresponding to a stable optimized configuration and bonding. The studied reactions are:



Since the energies of the organic radicals are required in equation (2), their structures were also optimized. The functionalization reactions (3) to (5) are thermodynamically favorable, as can be seen in Table 1, and the resulting binding energies are around 1 eV.

Dipole moments (μ_{dip}) and the Gibbs free energy of solvation (ΔG_{solv}) for the pure and functionalized SWCNT is displayed in Table 1 and from these computed electronic properties it can be seen clearly that there is a substantial increase in the value of the magnitude of the dipole moments of the functionalized nanotubes compared to the unfunctionalized nanotube. The large dipole moments of the functionalized SWCNT versus the infinite pure nanotube model which has practically no dipole moment suggests that this increase is expected to modify the functionalized nanotubes interaction with a polar solvent such as water, potentially increasing the dispersion of the SWCNTs in the physiological medium as discussed in the next section.

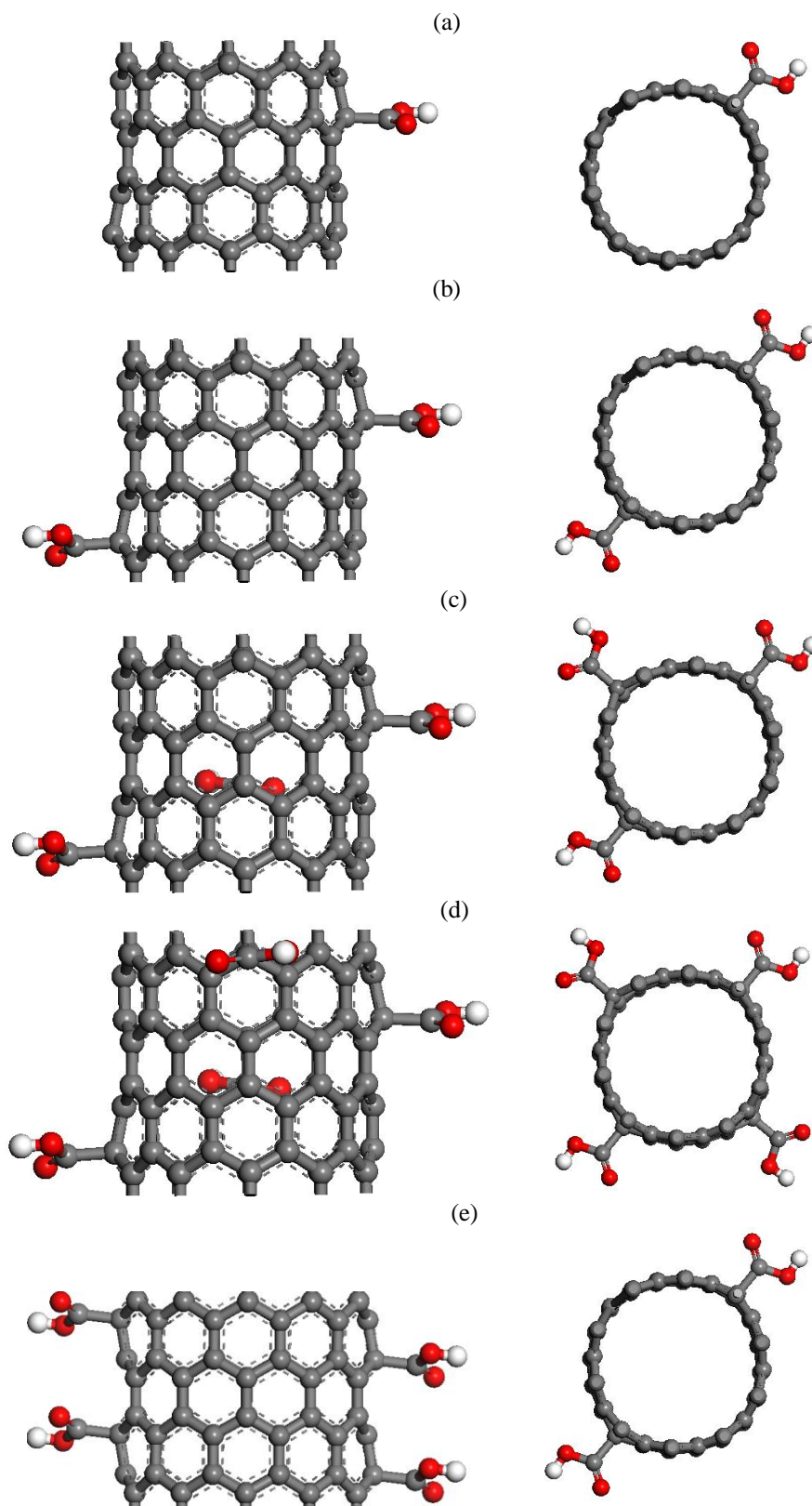


Fig.5. Functionalization density dependence; optimized geometry of the SWCNTs with the formic acid radical at the tube sidewall at: (a) 1.25%, (b) 2.50%, (c) 3.75 %, (d) 5.0% and (e) also at 5.0% addends. Gray color depicts carbon atoms; white is hydrogen, and red is oxygen.

3.2. Solubilization

Measuring its Gibbs free energy of solvation can assess solubility. The Gibbs free energy of solvation, ΔG_{solv} , is defined as

$$\Delta G_{solv} = E_{gas} - E_{COSMO} \quad (6)$$

where E denotes the computed optimized total energy of the species in the solvent (COSMO) and vacuum (gas phase). The COSMO takes into account simplification of the CSM approach without significant loss of accuracy. Because of this simplification, COSMO allows for a more efficient implementation of the CSM into quantum chemical programs and for accurate calculation of gradients, which allows geometry optimization of the solute within the dielectric continuum for the treatment of solvation effects as mentioned in the methodology section. A positive value of ΔG_{solv} for all the functionalized nanotubes, given in Table 1, indicates solubility in water. Specifically, a large ΔG_{solv} is obtained for the functionalized nanotubes in comparison for the value obtained for the unfunctionalized nanotube. On the other hand, the solvation Gibbs free energy for the SWCNT is 0.08eV, which is predicted to be insoluble. The solubility increases dramatically and substantially in all cases by using the technique of functionalization with the said organic acid radicals. Also all the calculated ΔG_{solv} of the functionalized nanotubes given in Table 2 suggests that as the degree of sidewall functionalization increases, the SWCNT sample becomes more and more soluble. These is in agreement with the experiment performed in vitro cytotoxicity screens on HDF by Sayes et al. [18] wherein the sidewall functionalized SWCNT with phenyl-SO₃H and phenyl-(COOH)₂ samples are found out to be substantially less cytotoxic than unfunctionalized SWCNT in water.

5 CONCLUSIONS

Using the *Dmol³* code, which uses periodic supercells and localized atom-centered basis set under the density functional theory formalism, we have verified that the solubility in water of SWCNT covalently functionalized with three different kinds of acids is improved. The nanotube has been functionalized with formic acid, isophthalic acid and benzenesulfonic acid. Electronic exchange and correlation effects have been treated with the gradient-corrected PBE functional.

The functionalization with these organic acid radicals on the nanotube sidewall was manifested not only by a stable optimized configuration but also with a strong binding energy and hence the covalent functionalization is said to be thermodynamically favorable. The enhanced dipole moment of the nanotubes due to functionalization is expected to modify its interaction with a polar solvent such as water, potentially increasing the dispersion of the SWCNTs as assessed by a positive value of solvation free energies of the functionalized nanotubes employing COSMO. Furthermore, it was established that as the degree of sidewall functionalization increases the SWCNT solubility also increases. Improved solubility reduces the toxicity and the chance of tissue accumulation of the nanotubes with a variety of biological components for future use.

TABLE 1

ELECTRONIC PROPERTIES FOR THE PURE NANOTUBE AND THE FUNCTIONALIZED SWCNT FORMED IN THE REACTIONS (3)-(5). THE PROPERTIES ARE: BINDING ENERGY (E_b), MAGNITUDE OF THE DIPOLE MOMENT (μ_{dip}) AND THE GIBBS FREE ENERGY OF SOLVATION (ΔG_{solv}) AT 1.25 % CONCENTRATION.

System	E_b (eV)	μ_{dip} (debye)	ΔG_{solv} (eV)
SWCNT	-	~0.00	0.08
CO ₂ H-SWCNT	0.67	3.60	0.31
C ₆ H ₃ (CO ₂ H) ₂ -SWCNT	1.24	3.96	0.54
C ₆ H ₄ SO ₃ H-SWCNT	1.13	3.80	0.47

TABLE 2

THE FUNCTIONALIZATION DENSITY DEPENDENCE OF SWCNTS GIBBS FREE ENERGY OF SOLVATION (ΔG_{solv}).

% Conc.	CO ₂ H -SWCNT (eV)	C ₆ H ₃ (CO ₂ H) ₂ -SWCNT (eV)	C ₆ H ₄ SO ₃ H -SWCNT (eV)
1.25	0.31	0.54	0.47
2.50	0.54	1.03	1.02
3.75	0.78	1.51	1.28
5.00	1.06	2.11	1.21

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