Journal of Molecular Liquids 212 (2015) 592–596

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Modeling of single-walled carbon nanotubes functionalized with carboxylic and amide groups towards its solubilization in water

Michael Mananghaya

De La Salle University, 2401 Taft Avenue, 0922 Manila, Philippines
DLSU STC Laguna Boulevard, LTI Spine Road Barangays Biñan and Malamig, Biñan City, Laguna, Philippines
Analysis of NAnomaterials (ANA) Division IX, National Research Council of the Philippines, General Santos Ave, Taguig, 1631 Metro Manila, Philippines

ARTICLE INFO

Article history:
Received 30 May 2015
Received in revised form 31 August 2015
Accepted 6 October 2015
Available online 11 November 2015

Keywords:
Binding energy
Density functional theory
Gibbs free energy of solvation
Single-walled carbon nanotubes

ABSTRACT

The paper discusses the impact of functionalization on understanding the solubility of a single-walled carbon nanotube (SWCNT) to increase its dispersion in water, with the aide of spin-unrestricted density functional theory (DFT). A finite (10, 0) zigzag nanotube model containing 80 C atoms saturated with hydrogen at the ends was investigated with DFT. The (10, 0) SWCNTs were functionalized with: (a) carboxylic acid, (b) aromatic dicarboxylic acid and (c) aminotriethylene glycol, which can be derived from the carboxylic acid. The functionalization is thermodynamically stable and bonding is favorable. The results show an enhancement in the solubility of the nanotubes in water due to increased dipole moment as visualized in the HOMO–LUMO surface plots. Further as the degree of sidewall functionalization increases, the SWCNT sample becomes more soluble as assessed by the calculated Gibbs free energies of solvation.

1. Introduction

The outstanding material properties of carbon nanostructures with respect to unique mechanical, optical, and electronic properties and its application are currently under study [1–15]. Specifically, carbon nanotubes (CNTs) can be used to deliver a variety of therapeutic agents, including biomolecules, to the target disease sites. The CNT has unparalleled optical and electrical properties, making them excellent candidates for Bioimaging and other biomedical applications. Nevertheless, the high cytotoxicity of CNTs limits their usage in humans and many biological systems [7–10]. The greatest advantage of nanotechnology lies in its potential to create novel structures with enhanced abilities to translocate through cell membranes, and increased solubilization, stability, and bioavailability of biomolecules, thereby enhancing its delivery efficiency. Nanotechnology offers intriguing opportunities for various applications in biomedical fields, including Bioimaging and targeted delivery of biomacromolecules into cells. The smooth surface of carbon nanomaterials lacking any overhanging bonds renders them chemically inert and incompatible with almost all organic and inorganic solvents, which further makes them less amenable to manipulation and downstream applications. In order to address this problem, surface modifications [11] or functionalization of nanoparticles could play a crucial role in improving their physicochemical and surface properties.

The overall objective of functionalizing CNTs for biomedical applications is to increase their solubility or dispersion in biocompatible aqueous media, thereby reducing toxic effects. It has been reported that after modifications, functionalized CNT (fCNT) solubility increased significantly [7–10] and alters their cellular interaction pathways, resulting in much-reduced cytotoxic effects [12–15]. The fCNTs are promising novel materials for a variety of biomedical applications. These potential applications are especially heightened by their power to penetrate biological membranes with relatively low cytotoxicity for effective employment in biomedical applications. The dispersion of multiwalled or single-walled carbon nanotubes (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 [7–10], [12–15]. The paper investigates the functionalization interactions between carbon nanotubes with carboxylic (COOH) and amide ($^{-}CONH_2$) groups based on computational simulation and modeling with the aide of density functional theory (DFT) calculations [16–18] to show improved solubility. Improved solubility permits applications such as miscibility in cell culture with satisfactory distribution, low aggregation and reduced cytotoxicity.

The accession of a layer of biocompatible material COOH can be used to wipe out the toxicity of pristine CNT aggregates by making them more dispersible in aqueous solutions. fCNTs can be achieved by using oligonucleotides, biomolecules, surfactants, and polymers, thus increasing the dispersibility of CNTs and decreasing their cytotoxicity. The water-dispersible properties of SWCNTs functionalized with different doping concentrations of acid groups change as a function of the degree of sidewall functionalization. Functionalization permits interaction with existing cells through miscibility in cell culture with satisfactory distribution, low aggregation and reduced cytotoxicity.

E-mail address: mikemananghaya@gmail.com.

http://dx.doi.org/10.1016/j.molliq.2015.10.013
0167-7322/

2. Methodology

The optimized structural geometry of (10, 0) single-walled carbon nanotube is presented in Fig. 1(a), the following is the assembly of acid-functionalized SWCNT with three organic groups. Namely, (a) formic acid, CO_2H_2, as a model of carboxylic acid, Fig. 1(b) [9–10]; (b) isophthalic acid, $C_6H_4(CO_2H)_2$, as a model aromatic dicarboxylic acid, consider Fig. 1(c) [18] and (c) aminotriethylene glycol, $C_7N_2O_3H_{16}$, as a model amide derived from the amidation reaction of the formic acid, consider Fig. 1(d). These organic molecules are investigated in hope for the design of species for efficient dispersion capability for drug delivery. All calculations were performed using a DFT with a B3LYP functional [19] and the computational cost is lowered by the use of highly localized grid representations wherein each electronic wave function is expanded in a localized atom-centered basis set with each basis function is defined numerically. For cluster geometries, spin-unrestricted calculations were carried out with a double numeric polarized (DNP) basis set available. Charge densities were analyzed by the Mulliken method [20]. For open-shell molecular radicals, the unrestricted formalism was used. The present level of calculation is known to produce reasonable results [21] for bond lengths, bond angles, and bond energies for a wide range of molecules. The inclusion of long-range correlation facilitates the accurate determination of van der Waals correction method wherein Tkatchenko–Scheffler (TS) was

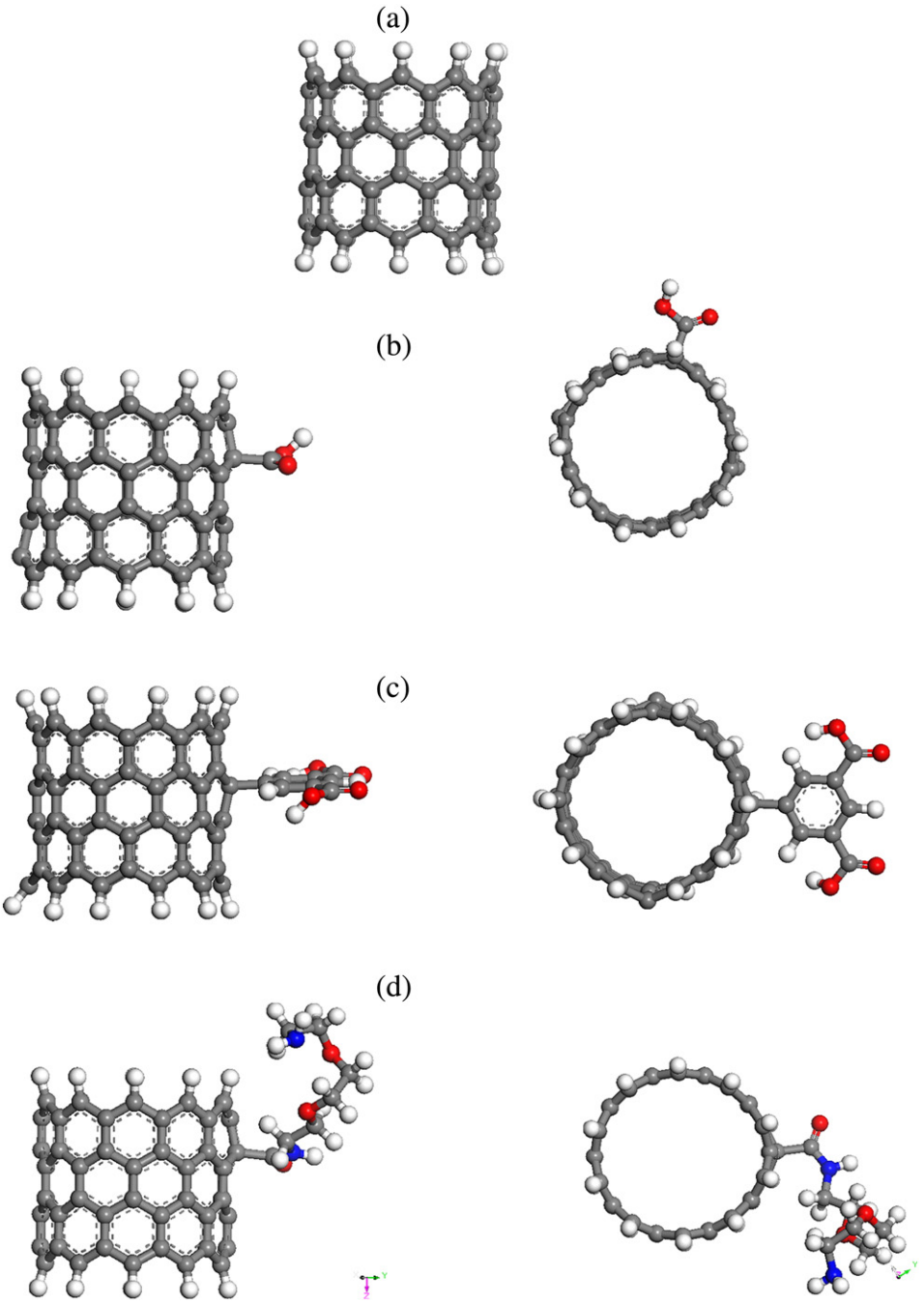

Fig. 1. Optimized geometry of the finite (a) (10,0) zigzag SWCNT; (b) (10, 0) zigzag SWCNT with the formic acid radical; (c) (10, 0) zigzag SWCNT with the isophthalic acid radical and (d) (10, 0) zigzag SWCNT with the aminotriethylene glycol acid radical at the tube sidewall in side view (left) and top view (right). Gray color depicts carbon atoms; white is hydrogen, nitrogen is blue and red is oxygen.