COMPUTER MODELING OF CHITOSAN ADSORPTION ON A CARBON NANOTUBE

Azimov J.T.
Academy of the Armed Forces of the Republic of Uzbekistan

Abstract: The article presents the results of modeling the process of adsorption of chitosan oligomer on a carbon nanotube (CNT). The results of calculating the structural properties of the monomer and dimer of chitosan using the density functional method to obtain optimal geometric parameters and charge distribution of chitosan are presented. Then, using classical molecular dynamics, the binding energy of the chitosan molecule and CNT is calculated. It is established that the nature of the interaction between the chitosan molecule and CNT is specific.

Keywords: carbon nanotube, chitosan, adsorption, molecular dynamics

Introduction

The widespread use of carbon nanotubes (CNTs) and other nanomaterials in electronics and biomedical applications, as biosensors and for drug delivery to living organisms, is hampered by the lack of knowledge about their behavior in vivo. Nanotubes are usually combined into bundles or bundles, and to prepare solutions they must be dispersed. There are two approaches to solving this problem: mechanical methods and methods that change the surface energy (both physical and chemical). Mechanical methods (e.g., ultrasonic treatment) separate nanotubes from each other, but can also damage them. Chemical methods use covalent functionalization of the surface to improve wettability or adhesion, but may introduce defects (e.g., using acids at high temperatures). In recent years, non-covalent functionalization of CNTs using surfactants or bioactive polymers has been widely used to prepare both aqueous and organic solutions [1]. Among such biopolymers, chitosan is of particular interest, since it is a type of polysaccharide and has a set of properties uniquely suitable for nanotechnology. The aim of this work is to study the structural and electronic properties of carbon nanotube complexes interacting with a chitosan molecule. To study the effect of chitosan molecules on the energy spectrum of CNTs, nanotubes with chirality (9, 0) and (11, 0) were considered. The structural properties of the CNT-chitosan complex were studied using molecular dynamics. The change in the electrostatic potential at the interface of CNTs and chitosan was investigated. The adsorption conditions and stability of the chitosan CNT complex were analyzed at different temperatures and pressures. Calculations of the electronic structure of nanotubes were performed in the local approximation of the density functional theory using the OPENMX software package [2]. The change in the electronic spectrum of CNTs during interaction with the chitosan molecule was studied, depending on the chirality of the nanotubes.

The relationship between nanotubes and the matrix

The potentially outstanding mechanical and electrical properties of carbon nanotubes are of little value unless they are embedded in a matrix. In obtaining nanotube-reinforced composites, two issues need to be addressed - the wetting process of the nanotube surfaces and the effect of chemical action. In the course of research, it became clear that some materials enter the open nanotubes faster than others. In any case, whether the liquid enters the core of the nanotube or not depends largely on the interfacial surface energy. If the contact angle at the liquid-solid interface is less than 900, the liquid will enter the tube spontaneously, but if the angle is greater than 90, the liquid will not enter the tube. Colleagues from NEC (see [3]) studied the wetting of nanotubes with various materials, trying to determine the "critical" surface energy below which wetting occurs. They concluded that the surface energy cutoff lies between 100 and 200 mN/m. Thus, water with a surface energy of about 72 mN/m is expected to enter the nanotubes by itself, as well as most organic solvents whose surface energy is lower than that of water. Metals like nickel wet these surfaces rather weakly. So, the wetting of untreated nanotubes by aluminum metal, which has a surface energy of about 840 mN/m, should be weak. On the other hand, in the work of Ajoyan and colleagues (see [3]), it was shown that nanotubes can be easily wetted by molten vanadium oxide (surface energy of about 80 mN/m). When

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 13 Issue: 12 in December-2024
https://www.gejournal.net/index.php/IJSSIR

the surface characteristics of the matrix material are unfavorable, the wetting of nanotubes can be improved by chemical treatment. This idea has been used by several groups of scientists. Malcolm Green's Oxford group showed that palladium ions interact strongly with nanotubes exposed to nitric acid. Similarly, Ebessen and colleagues showed (see [3]) that the deposition of uranium, yttrium and other metallic species on the surface of carbon nanotubes can be improved if the tubes are pre-oxidized. Of course, it must be recognized that chemical functionalization of nanotube surfaces will inevitably affect their mechanical properties. It was found in molecular dynamics simulations of the effect of covalent chemical attachments on the stiffness of single-walled nanotubes that covalent chemical attachments reduce the maximum bending force by 15% regardless of the helical tube structure or radius. Considering the extremely high Young's modulus of the nanotubes, a 15% reduction in stiffness is not catastrophic and suggests that functionalization can be used to anchor the tubes in the matrix without significant losses in mechanical properties.

Aspect Ratio

In order to make the most of the fibre stiffness in a composite, it is necessary to achieve the maximum fibre stress (i.e. the stress at which it fails) when applied transversely. Thus, to obtain the maximum stress state, the fibres must have a certain minimum aspect ratio (length to diameter ratio). The minimum ratio required for maximum stress transfer is given by l_c / d, where l_c is the critical fibre length and d_C is the diameter. Kelly (see [3]) showed that for a unidirectional composite, this ratio is given by

$$\frac{l_c}{d} = \frac{\sigma_{\max}}{2\tau}$$

Where τ is the transverse stress at the interface. So the stronger the fibers, the longer they must be for the stress to reach its maximum value at a given diameter. A value of about 100 GPa can be taken as the fracture stress of nanotubes, 50 MPa as the transverse stress of a conventional polymer, at a diameter of 10 nm, we get an aspect ratio of 1000:1.

Biomodification of carbon nanotubes

The methods used for direct and indirect modification with biopolymers are divided into three classes depending on the nature of how biomolecules bind to carbon nanotubes: covalent attachment (formation of a chemical bond), non-covalent attachment (physical absorption) and a hybrid approach [4].

The main simple method for covalent functionalization of carbon nanotubes is reaction with carboxylic acid moieties (-COOH) on carbon nanotubes. These carboxylic acid groups are usually introduced by oxidation using strong acids, and they preferentially occupy the more reactive (open) ends or defective sides of single-wall and multi-wall carbon nanotubes than their sidewalls. Nitrile cycloadditives, arylation with diazonium salts or 163-dipolar cycloadditives are commonly used for sidewall functionalization of carbon nanotubes. The large aromatic (pi electrons) hydrophobic surface area of carbon nanotubes makes them ideal partners for non-covalent interactions with suitable complementary molecules and macrobiomolecules. These interactions take place both outside and inside the carbon nanotubes. These interactions are typically hydrophobic in nature and non-specific, but are readily applicable to many biomolecules including heavy metal-doped DNA and polysaccharides such as helical amylose. Strong non-covalent interactions between nanotubes and certain aromatic and/or hydrophobic molecules can also be exploited to provide a platform for further functionalization with biomolecules.

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 13 Issue: 12 in December-2024
https://www.gejournal.net/index.php/IJSSIR

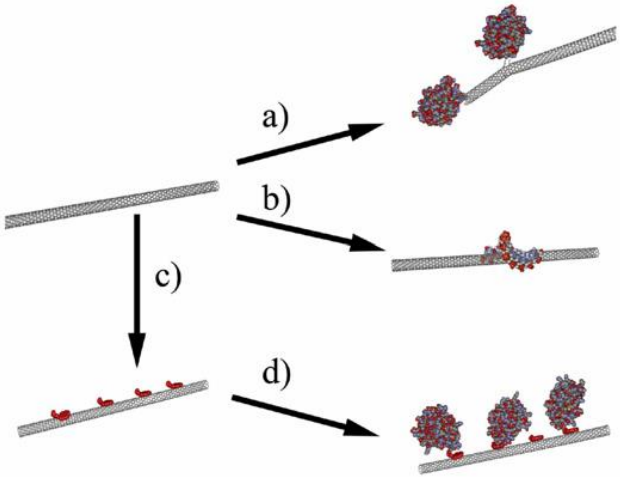


Fig. 1. Biomolecules bound to carbon nanotubes

The main advantage of non-covalent and hybrid approaches is that the structure of carbon nanotubes is not significantly altered in contrast to the covalent chemical approach (especially upon oxidation) [4]. This facilitates the comparison of properties such as conductivity before and after biomodification. The main drawback of these methods is the lack of specificity and in some cases denaturation of the biomolecule upon adsorption. Further, the biomolecule can completely encapsulate the tube, which can be an advantage as shown by Wallase et al. (see [4]), where chitosan and hyaluronic acid polysaccharides were used to help with the dispersion of the tubes, which were then used to produce carbon nanotube biofibers with strong enhancement of mechanical properties compared to other methods for spinning carbon nanotube fibers.

Electrochemical Biosensors

A particular advantage of carbon nanotubes for biomolecule integration is their small size, allowing these nanoelectrodes to be inserted into places where electrochemistry cannot work, such as inside proteins [5]. One possibility that carbon nanotubes offer is an efficient way to communicate with the environment of a biomolecule as biosensors. Typically, such communication is achieved through electron transfer. The potential of carbon nanotubes to facilitate communication between enzymes and the external environment with efficient electron transfer can be demonstrated by the example of glycose oxidase, DNA, and other enzymes [5].

Chitosan/Carbon Nanotube Composites

Of great interest to us is the production of chitosan-carbon nanotube composites. We know that covalent and non-covalent functionalization of nanotubes and their dispersion in a polymer matrix is not very effective. Recently, a carbon nanotube-based film has been prepared by layer by layer, which can eliminate the problem of poor solubility of nanotubes. Another advantage of this method is the simplicity of the process and the wide choice of materials. Chitosan, a natural biopolymer, exhibits high compatibility with water, good adhesion, and solubility in slightly acidic solution [5,6]. Due to the solubility of chitosan in slightly acidic medium, the amino and hydroxyl groups of chitosan are protonated with a positive charge [6]. Therefore, chitosan has the ability to be modified by other agents. A multilayer stable and one-dimensional film based on chitosan and carbon nanotubes can be easily obtained based on the electrostatic interaction between the negatively charged nanotube and the positively charged chitosan biopolymer. The electrochemical catalytic activity of such electrodes based on such a multilayer film has been revealed. This electrode was very stable and had a fast and sensitive response to the electrochemical oxidation of the coenzyme dihydronicotinamide adenine dinucleotide. In these experiments, carbon nanotubes were chemically modified in sulfuric and nitric acids. Thus, the chitosan-nanotube based multilayer films have potential applications for the development of a series of dehydrogenase-based biosensors. In addition,

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 13 Issue: 12 in December-2024
https://www.gejournal.net/index.php/IJSSIR

such composites were prepared based on the solution-evaporation method [7]. Compared with pure chitosan, the mechanical properties, including tensile modulus and tensile strength, of the nanocomposites are greatly increased by 93% and 99%, respectively, with the incorporation of carbon nanotubes at only 0.8wt % into the chitosan matrix. However, although the use of strong oxidizing agents is effective, it introduces defects into the nanotubes, which is undesirable since it may lead to deterioration of the electrical and mechanical properties. Collaborators from Hong Kong Polytechnic Univ. and Shanghai Inst. Materia Medica (China) [8] developed a method of non-covalent modification that does not damage the original surface of nanotubes. They used the biopolymer chitosan. The method is shown schematically in Fig. 2.

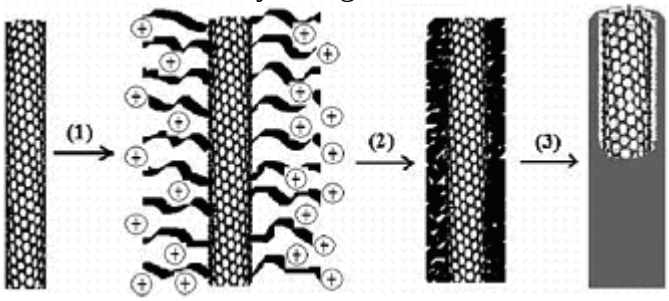


Fig. 2. Scheme of the process of decorating the surface of MWCNTs with chitosan.

The developed method uses the emulsifying ability of chitosan, its completely different solubility in acidic and alkaline aqueous solutions and behavior in the polymer cross-linking reaction. It is hoped that, due to the combination of the unique properties of CNTs and biocompatible chitosan, such decorated CNTs will find wide application in chemistry, biology and medicine as biosensors and suppliers of genes and drugs to the body.

Details of computer modeling

The structural properties of chitosan and nanotubes were studied using classical molecular dynamics. To calculate the energy of the system, the Lennard-Jones potential was used and the electrostatic forces were calculated by the Coulomb potential:

$$V_{ij}(r_{ij}) = V_{ij}^{el}(r_{ij}) + V_{ij}^{LJ}(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

The carbon nanotube was placed in the center of a cubic box measuring 30X30X30 A and the chitosan molecules were located near the nanotube at a distance of 8-10 A from the line passing through the center of the nanotube (Fig. 3). After that, the cubic box was filled with water molecules, preliminarily relaxed to the equilibrium state. Since the chitosan molecule is protonated and has a positive charge, negative Cl- ions were added to the system for neutralization. In calculating the free energy of dissolved molecules for water, an improved simple point-charged (SPC/E) model was used, which describes well the structural and thermodynamic properties of pure water in wide ranges of temperatures and pressures. The covalent bond length of oxygen and hydrogen atoms is fixed at 1.0 Å and the bond angle is 109.47^0, so that the geometry of the SPC/E water model is represented as a rigid structure with partial charges of oxygen atom -0.8476e and hydrogen +0.4238e.

The structure of chitosan was optimized by the Moller-Posset (MP2) method (see Section 1) and 6-31G** were chosen as the basis wave functions. The results of quantum chemical calculations were used to calculate the charge distribution of the chitosan molecule by the electrostatic potential method (RESP). The Lennard-Jones interaction parameters were determined by the Lorentz-Berthelot rule. The calculations were carried out at constant pressure and temperature with the Berendsen barostating and thermostatting algorithm in a cubic box filled with 3000 water molecules.

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 13 Issue: 12 in December-2024
https://www.gejournal.net/index.php/IJSSIR

The equations of motion were solved by the Verlet algorithm with a time step of 1 fs. Long-range Coulomb forces were calculated using the Ewald method (RME) with an accuracy of 1X10-6 and all intermolecular interactions inside the box were calculated inside a sphere with a radius of Rcutoff=9 A. The equilibrium state of the system was reached in 50 ps time and this procedure was repeated for each system before calculating the thermodynamic parameters.

Fig. 3 shows a system simulated by the molecular dynamics method: a nanotube and chitosan molecules.

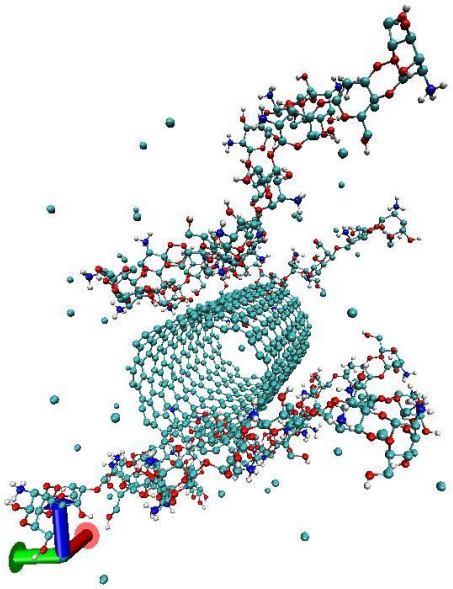
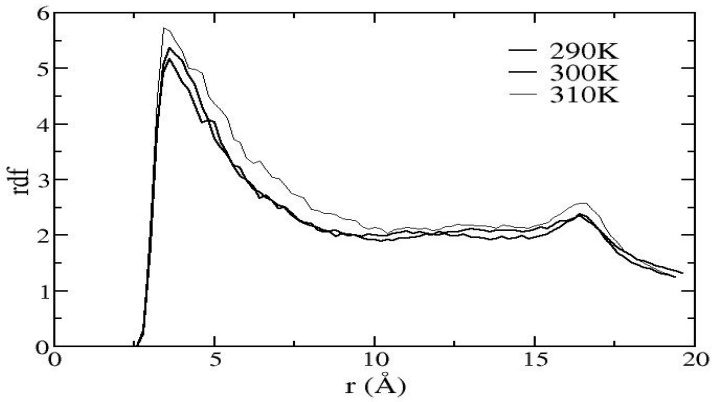
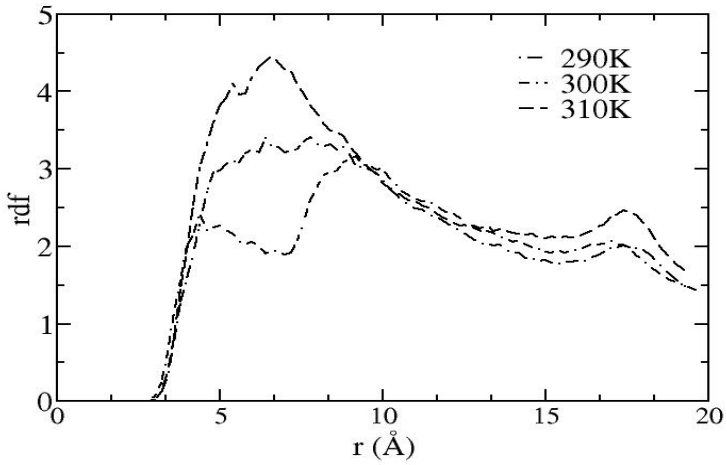


Fig. 3. Nanotube and chitosan molecules in a box



a)

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 13 Issue: 12 in December-2024
https://www.gejournal.net/index.php/IJSSIR



b)

Fig.4. Radial distribution functions

Fig. 4 a and b show the radial distribution functions OS of oxygen (a) and the N atom of chitosan with a nanotube. The results show that CNT mainly interacts with two groups of chitosan - oxygen from the CH2OH group and nitrogen of the amide group. Moreover, the equilibrium distance between CNT and oxygen is about 5 Å, and between CNT and nitrogen is about 6 Å. With a change in temperature, the radial distribution changes noticeably for the case of interaction of CNT with nitrogen, namely, with a decrease in temperature, two equilibrium distances appear - 6 and 10 Å.

Conclusion

The energy and structural characteristics of the nanocomposite based on CNT and chitosan were studied using the molecular dynamics method in the Gromacs program. The total, kinetic and potential energies of such a system were obtained. The radial distribution functions of chitosan with a nanotube were analyzed. The results show that CNT mainly interacts with two groups of chitosan - oxygen from the CH2OH group and nitrogen of the amide group. Moreover, the equilibrium distance between CNT and oxygen is about 5 A, and between CNT and nitrogen is about 6 A. When the temperature changes, the radial distribution changes noticeably for the case of interaction of CNT with nitrogen, namely, when the temperature decreases, two equilibrium distances appear - 6 and 10 A.

Literature

1. L.Vaisman, Adv. Colloid Interface Sci. 128-130, 37 (2006).
2. T. Ozaki, Phys. Rev. B. 67, 155108, (2003).
3. Харрис П. Углеродные нанотрубы и родственные структуры, Пер. с анг. Под ред. Чернозатонского Л.А., Техносфера, Москва, 2003, 335с.
4. W.Yang, P. Thordarson, J. Gooding, S. Ringer and F.Braet, Carbon nanotubes for biological and biomedical applications, Nanotechnology 18 (2007), 412001
5. H. Yi et al. Biofabrication with chitosan, Biomacromolecules, v.6, N 6, 2881 (2005)
6. X.Zhai, W.Wei, J.Zeng, S.Gong and J.Yin, Layer-by-Layer assembled film based on chitosan/carbon nanotubes, and its application to electrocatalytic oxidation of NADN, Microchim Acta 154, 315-320 (2006)
7. S. Wang, Lu Shen, W. Zhang, Y.Tong, Preparation and echanical properties of chitozan/carbon nanotubes composites, Biomacromolecules 6 (6), 3067-3072, 2005
8. YY Liu, J Tang, XQ Chen, J H Xin*. Decoration of Carbon Nanotubes with Chitosan, *Carbon*, 2005, 43, 3178-3180.

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 13 Issue: 12 in December-2024
https://www.gejournal.net/index.php/IJSSIR