Investigation of the interactions between molecules of β-Carotene, Vitamin A and CNTs by MD simulations

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A B S T R A C T

Two typical phenomena (wrapping and filling), mainly about the interactions between biological molecules and carbon nanotubes (CNTs), were investigated by performing molecular dynamics (MD) simulations. We calculated the center of mass (COM) distance and the interaction energy between the biological molecules and single-walled nanotubes (SWNTs). The influence of nanotube wall number, chirality, radius and temperature was also investigated by a series of MD simulations. The results indicated that Vitamin A and β-Carotene were two promising biomaterials for decoration of CNTs. The interactions between biological molecules and CNTs could be influenced by those four factors. The general conclusions derived from this study may be of importance in medical and biological areas.

1. Introduction

In recent years, owning to the unique properties of carbon nanotubes (CNTs), many researchers have been focusing on this intriguing topic. Two different methods, chemical modification and physical modification, towards the preparation of soluble CNTs have been proposed, both of which reduce a large extent of the toxicity of CNTs and expand their safe use in the fields of nanobiotechnology and nanomedicine.

Using molecular dynamics (MD) simulations, Gao and his coworkers had reported that a DNA molecule in a water solute environment could be spontaneously filled into a CNT [1], Raczyński and his coworkers had made simulations of the system composed of single-walled nanotube (SWNT) surrounded by some cholesterol molecules [2], etc. Carotenoids are very important natural pigments in plants and animals and a series of experiments [3–5] had been conducted to investigate the β-Carotene molecules encapsulated in CNTs. Under ambient conditions, β-Carotene can easily degrade into Vitamin A. In this study, using MD simulations, we investigated these two biological molecules interacting with outer walls of CNTs or filling into CNTs. Take β-Carotene as an example, the influence of nanotube wall number, chirality, radius and temperature on the interactions between biological molecules and CNTs were studied.

2. Simulation details

MD simulations were conducted long enough mainly on two processes: wrapping and filling using a commercial software package called Materials Studio (MS) developed by Accelry Inc. Since we only studied the interactions between the CNTs and biological molecules, we located all models in vacuum to eliminate the influence of the solvents. Except for some special conditions, a constant temperature of 300 K was kept and the NVT ensemble was used in each simulation. The force-field used here was the COMPASS force-field. As shown in Fig. 1, the molecular structures of β-Carotene (96 atoms, 536) and Vitamin A (51 atoms, 286) were established using MS. β-Carotene and Vitamin A are both π-conjugated molecules and both of them can...
exhibit π–π interaction with SWNT. Using MS, energy-minimization molecular mechanics (MM) were performed to find the thermal stable morphology and achieve a conformation with minimum potential energy for all models.

3. Results and discussions

3.1. Wrapping

As a promising way for manipulating and organizing SWNTs into ordered structures and improving their dispersion into the matrix of the composites, the wrapping of CNTs has received extensive attentions. Two biological molecules were initially arranged at the side of a (30, 0) SWNT respectively with a distance of approximately 0.5 nm.

Van der Waals forces which exist between molecules are the primary forces in our simulated systems. The bigger the molecule is, the stronger the van der Waals forces are. During the simulations, two molecules gradually orientated to align their ring planes parallel to the SWNT surfaces. As shown in Fig. 2(a), the center of mass (COM) distance between the biological molecule and SWNT indicated that it cost about 140 ps for the wrapping of β-Carotene but only 30 ps for Vitamin A to achieve the equilibrium. This was because the shorter chain of Vitamin A made its atoms have smaller resistance from adjacent atoms. The distances between the COM of biological molecules and the nanotube walls were about 0.32 nm for β-Carotene and about 0.35 nm for Vitamin A.

The interaction energy can demonstrate the dynamic behavior of the biological molecules. It is estimated from the energy difference between the total energy of composite and the sum of the energies for the biological molecule and the corresponding SWNT as follows:

\[ \Delta E = E_{\text{total}} - (E_{\text{SWNT}} + E_{\text{biological molecule}}). \]

where \( E_{\text{total}} \) is the total energy of the composite, \( E_{\text{SWNT}} \) is the energy of the nanotube without biological molecule, and \( E_{\text{biological molecule}} \) is the energy of biological molecule without SWNT [6]. Fig. 2(b) showed the interaction energies during the wrapping process. Since β-Carotene had more conjugated bonds throughout its molecule, it exhibits stronger π–π interaction with SWNT. The interaction energy for β-Carotene (about −47.81 Kal/mol) was higher than that for Vitamin A (about −26.07 Kal/mol).

The interaction energies between β-Carotene and (30, 0) CNTs with different wall numbers during the wrapping process were studied. As shown in Fig. 2(c), with increasing wall number the intermolecular interaction energy increased and the time...
gradually move their whole bodies into nanotubes. The accord with the experimental investigation[4]. It could be the π direction of the nanotube axis with an approximately 0.3 nm distance respectively.

reactive species [7]. In this study, two biological molecules were placed along the reported that the organic molecules inside the tubes can be protected from any external applications of CNTs in drug delivery, nanocontainer and so on. Takenobu et al. have described processes.

3.2. Filling

The possibilities of filling molecules into nanotubes arouse great interest in applications of CNTs in drug delivery, nanocontainer and so on. Takenobu et al. have reported that the organic molecules inside the tubes can be protected from any external reactive species [7]. In this study, two biological molecules were placed along the direction of the nanotube axis with an approximately 0.3 nm distance respectively.

We could observe that the molecular chains of β-Carotene and Vitamin A would gradually move their whole bodies into nanotubes. The β-Carotene, a one-dimensional π-conjugated molecule, was aligned to the SWNT axis after encapsulation, which is in accord with the experimental investigation [4]. It could be the π–π interaction that shifts the encapsulated biological molecule off the center of the SWNT. The decrease of the COM distance in Fig. 3(a) showed that it cost about 210 ps for the filling of β-Carotene but only 90 ps for Vitamin A to achieve an equilibrium state. The distances between the COM of biological molecules and the nanotube walls were about 0.46 nm for β-Carotene and 0.44 nm for Vitamin A. This was also quite similar to the Yanagi et al.’s experimental results (0.4 nm).

Fig. 3(b) showed the interaction energies during the simulations. Just as the process of wrapping, once they started inserting into the nanotube, the interaction energies increased rapidly, which revealed that the filling could significantly improve the load transfer between biological molecules and SWNTs. The interaction energy for SWNT-β-Carotene was about ~64.69 Kal/mol and for SWNT-Vitamin A was about ~34.30 Kal/mol. We also noticed that the time consumption of Vitamin A to achieve the equilibrium was much shorter than that of β-Carotene due to its shorter chain.

Take β-Carotene as an example, we further explored the influence of another three factors: chirality, temperature and radius. After each system had reached an equilibrium state, we calculated the interaction energy every 10 ps for 20 times and took the average to get rid of fluctuations.

We examined the effects of chirality and temperature in five distinct systems. The temperatures were varied from 250 to 450 K in steps of 25 K. Each type of SWNT in five systems had similar molecular weights, diameters and lengths. As shown in Fig. 4, the armchair CNT was always the best type for interaction, which agreed well with the former results [6]. In addition, we found that the intermolecular interactions decreased for (30, 0), (27, 5), (24, 10), (20, 15) with increasing temperature. However, the interaction for (17, 17) did not exhibit obvious tendency with increasing temperature, so the temperature influence could be negligible for armchair nanotube. The influence of radius was also considered. The intermolecular interaction between the β-Carotene and SWNT exhibited a fluctuating decreasing trend with increasing radius which suggested the possibility of a best radius for the simulated systems.

4. Conclusion

Some MD simulations were conducted to investigate the interactions of β-Carotene and Vitamin A molecules with CNTs and all models could achieve a typical equilibrium state by MD simulations. β-Carotene and Vitamin A were two promising biomaterials for decoration of CNTs. The simulations also showed that the interactions between biological molecules and CNTs could be influenced by four factors: nanotube wall number, chirality, radius and temperature, thus we should properly select or set them to ensure a successful manipulation. The general conclusions derived from this study may be of importance in medical and biological areas.

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References