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Charge-tunable insertion process of carbon nanotubes into DNA nanotubes

Lijun Liang[a,b], Zhisen Zhang[c], Zhe Kong[d], Yong Liu[e], Jia-Wei Shen[e,*], Debing Li[a], Qi Wang[b,*]

[a] College of Life Information Science and Instrument Engineering, Hangzhou Dianzi University, Hangzhou, People's Republic of China
[b] Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
[c] Research Institute for Soft Matter and Biomimetics, Department of Physics, Xiamen University, Xiamen 361005, People's Republic of China
[d] College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, People's Republic of China
[e] School of Medicine, Hangzhou Normal University, Hangzhou 310016, People's Republic of China

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ABSTRACT

Control over interactions with biomolecules holds the key of the applications of carbon nanotubes (CNTs) in biotechnology. Here we report a molecule dynamics study on the encapsulation process of different charged CNTs into DNA nanotubes. Our results demonstrated that insertion process of CNTs into DNA nanotubes are charge-tunable. The positive charged CNTs could spontaneously encapsulate and confined in the hollow of DNA nanotubes under the combination of electrostatic and vdW interaction in our *ns* scale simulation. The conformation of DNA nanotubes is very stable even after the insertion of CNTs. For pristine CNTs, it could not entirely encapsulated by DNA nanotubes in simulation scale in this study. The encapsulation time of pristine CNTs into DNA nanotubes was estimated about 21.9 s based on the potential of mean force along the reaction coordination of encapsulation process of CNTs into DNA nanotubes. In addition, the encapsulation process was also affected by the diameter of CNTs. These findings highlight the charge-tunable self-assembly process of nanomaterials and biomolecules. Our study suggests that the encapsulated CNTs-DNA nanotubes could be used as building blocks for constructing organic–inorganic hybrid materials and has the potential applications in the field of biosensor, drug delivery system and biomaterials etc.

1. Introduction

Organic–inorganic hybrid materials do not represent only a creative alternative to design new materials and compounds for academic research, but their unusual features also promote the development of innovative industrial applications [1–3]. Recently, DNA nanotechnology has aroused much attention since its inception work by Seeman in 1982 [4]. Self-assembly nanotubes made from carbon [5–8], peptide [9–11] and DNA [12–15] has been thought as the potential building blocks for constructing the larger hierarchical structure. With the development of the self-assembly technology, the DNA nanotubes structure with particularly precise control have been fabricated [16–19]. It provides a new era to construct active materials with controlled nanoscale motion, dynamics and reconfiguration [20]. Especially, the functionalization of DNA nanotubes has been developed to serve as the templates for the assembly of the other materials [21,22]. However, the enhancement of mechanical property of DNA nanostructure is necessary to expand the scope of its potential applications [20,23–25]. For example, the improved resolution in force spectroscopy to detect DNA-protein interaction could be obtained with the improvement of the mechanical property of DNA nanostructure [26]. One way to enhance the mechanical property of DNA nanotubes is to make them composite material, and it could be achieved if DNA nanotubes hybrid with inorganic material.

Carbon nanotubes (CNTs) has attracted considerable attention due to its unique electric and mechanical properties from its first discovery in 1991 [27]. Extension research on application of CNT-based materials including nano-electronics, energy-storages, biotechnology and medicinal chemical has shown tremendous promises that CNTs could serve as an excellent building block [28–31]. Especially, CNTs have been used as building blocks to fabricate room temperature field-effect transistors [32], diode [33] etc.

* Corresponding authors.
E-mail addresses: shen.jiawei@hotmail.com (J.-W. Shen), qiwang@zju.edu.cn (Q. Wang).

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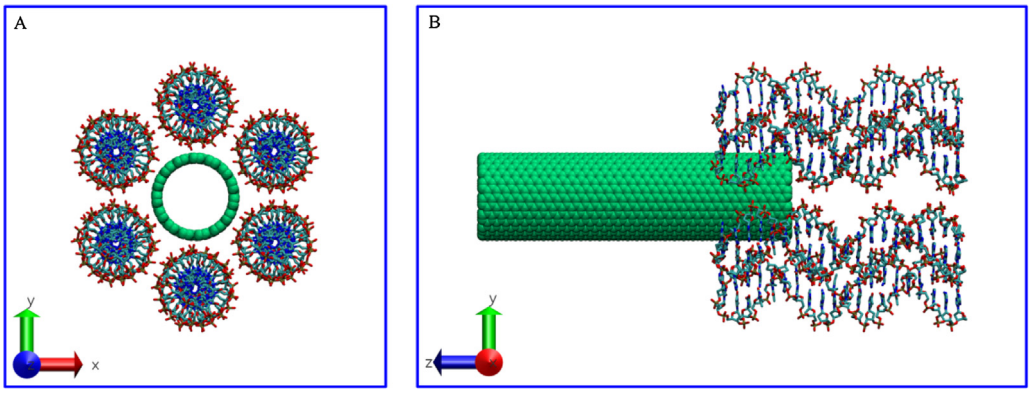

Fig. 1. Initial structure for CNTs (15, 15) in the DNA nanotubes. (A) the top view; (B) the side view. The DNA molecules are shown by CPK and ribbon model, and CNT are show in vdW model with green color. The water molecules and ions are not shown for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Many studies both from experimental [34,35] and theoretical works [36,37] have been explored on the interaction of CNT and DNA. These works greatly enhance our understanding of the properties of CNT in the interaction between CNT and DNA. In addition, both of CNT and DNA nanotubes have been investigated as drug delivery in recent years [38,39]. However, as two important building blocks for novel organic–inorganic hybrid materials, the interaction between CNT and DNA nanotubes at the molecular level are still obscure. Especially, the dynamics of self-assembly process of DNA nanotubes and CNTs need to be better understood, which is very crucial for hybrid CNT-DNA nanotubes materials as a building block for novel organic–inorganic materials. Herein, we report a molecular dynamics simulation study on the dynamics of encapsulation process of CNTs into the hollow of DNA nanotubes in a water soluble environment. Our results demonstrated that insertion process of CNTs into DNA nanotubes are charge-tunable. The positive charged CNTs could spontaneously encapsulate and confined in the hollow of DNA nanotubes under the combination of electrostatic and vdW interaction but not neutral CNTs in our ns scale simulation. The time scale of insertion process of neutral CNTs into DNA nanotubes is estimated based on the potential of mean force (PMF). In addition, the structure of DNA nanotubes is very stable even after the encapsulation of CNTs into its hollow.

2. Methods

2.1. System setup

The armchair (6, 6) and (15, 15) CNTs were constructed by visual molecular dynamics (VMD) tool [40]. The diameters of two CNTs are 0.81 nm and 2.03 nm with the length of 8.00 nm, respectively. The vertical axis of two CNTs is along z direction. The surface charge densities considered in this work are rather realistic; for example, depending on the fabrication procedures [41], the charge density of a silica surface can vary between 0 and -5 e/nm^2. The charge density modified carbon-based materials had also been used in other theoretical works [42,43]. Both two types of CNTs were modified with different charge density (σ) varied from $\sigma = -0.5$ e/nm^2 for negative CNTs to $+0.5$ e/nm^2 for positive CNTs. Here, e denotes the charge of a proton. The charge density $\sigma = q/A$, where q is the total charge in the modified CNTs, and A represents the surface area of modified CNTs. With different size of CNTs diameter, the surface area in CNT (6, 6) and CNT (15, 15) is different. The total charges were $-13e$, $0e$ and $13e$ in the systems with negative, pristine and positive CNT (6, 6) before adding water and counterions. The charges were $-45e$, $0e$ and $45e$ in the systems with negative, pristine and positive CNT (15, 15) before adding water and counterions.

Double strands DNA (dsDNA) molecule with the sequence of poly(AT)$_{20}$ was constructed by Hyperchem (Version 7.0, Hypercube, Inc), and it was equilibrated for 1 ns in vacuum. The hexamer DNA nanotubes are designed based on DNA origami object, as shown in reference [44]. The center-of-mass (COM) of all six DNA molecules were placed in one regular hexagon in x-y plane, and the side length of regular hexagon is 2.31 nm. Na^+ ions or Cl^- ions was added into the water box to neutralize the system. Then 100 ns *NVT* ensemble simulation were performed to equilibrate the system. The structure of hexamer DNA nanotubes at the final state of the equilibration was exacted as the initial structure for investigating the encapsulation process of CNTs into DNA nanotubes. Position restrains of DNA nanotubes in x, y and z dimensions were used, and the force constant is 50 kJ mol^{-1} nm^{-2}. To investigate the effect of restrains of DNA nanotubes in the simulation, the simulaiton including DNA nanotubes without the restrains was also performed. The vertical axis of DNA nanotubes coincides with the vertical axis of CNTs, which is z axis. To accelerate the insertion process, 1.0 nm length of CNTs was inserted into the DNA nanotubes at the beginning of the equilibration, as shown in Fig. 1B. In most cases, the water box is $10.00 \times 10.00 \times 21.00$ nm^3 in the x, y and z directions, and 49566 TIP3 P water molecules were added into the box with system density of 1.001 g/cm^3. The buffer lenghs is 4 nm in z directon, and it is long enough to avoid the interaction with its periodic image. At last, Na^+ or Cl^- ions were added into the solution to neutralize the system, and the total atoms are around 157,000.

2.2. System simulation

The DNA molecules, Na^+ and Cl^- ions were modeled by the Charmm27 force field. The force field parameters of carbon atoms in CNTs were $\sigma_{CC} = 0.385$ nm and $\varepsilon_{CC} = 0.439$ kJ mol^{-1}, as used in previous works [45–48]. All atoms including hydrogen atoms were represented explicitly, and the bonds with hydrogen atom were constrained by LINCS algorithm. The cutoff for the non-bonded van der Waals interaction was set by a switching function starting at 1.0 nm and reaching zero at 1.2 nm. The Particle mesh Ewald (PME) summation [49] was used to calculate the long-ranged electrostatic interactions, with a cutoff distance of 1.2 nm for the separation of the direct and reciprocal space. All simulations were performed by Gromacs-5.0.4 program with the time step of 2 fs. Periodic boundary conditions (PBC) were applied in all MD simulations. After 10 ns equilibration, all MD simulations were carried out in NPT ensemble, and the Langevin method was employed to keep the temperature at 298 K and the pressure at 101.3 kPa, respectively.