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Injection of stored nucleotides from single-walled carbon nanotubes

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Abstract: We investigate the possibility of injection of a nucleotide via single-walled carbon nanotubes (SWNTs). The collapse process of an SWNT with a large radius may proceed like falling dominoes. The characteristics of a large radius SWNT are utilized to drive the nucleotide movement in the SWNT, or even to inject the stored nucleotide out of the SWNT. In this process, the lateral section of the collapsed SWNT resembles a dumbbell. Occasionally, the nucleotide in the SWNT will be inbreathed into one of the two dumbbell ends, leading to interference with the injection process. To investigate the random nature of the injection process, a series of simulations on SWNT with different lengths were carried out. It was found that the injection probability was not influenced by the tube length. Freezing the nucleotide at the beginning, or modifying the SWNT at the outlet, may serve to facilitate the injection process, as indicated by the rise in the injection probability.

Key words: Nano injection, Single-walled carbon nanotube (SWNT), Nucleotide
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1 Introduction

The carbon nanotube (CNT) has been widely used in transportation of small atoms or molecules, such as helium (Wang, 2009), water (Joseph and Aluru, 2008; Liu *et al*., 2009), and RNA (Yeh and Hummer, 2004), due to its low frictional barrier (Falvo *et al.*, 1999; Kolmogorov and Crespi, 2000; Li and Yang, 2007). Advanced techniques have been developed to fabricate a nanogun shooting fullerenes via a single-walled carbon nanotube (SWNT) (Chang, 2008; Dai *et al*., 2008). Some of these techniques shoot the small molecule by virtue of charging the SWNT (Dai *et al*., 2008). Others utilize deformation, such as the torsion buckling, or a domino process of the SWNT, to push the fullerene out (Chang, 2008; Duan and Wang, 2010). The latter technique, the domino process, is employed herein to inject the stored nucleotide. Substantial simulations are carried out to explore the influence to this injection process from tube length, temperature, and modification on the tube.

2 Method

To investigate the potential of the injection based on the SWNT, a simulation system is set up (Fig. 1, see p.3). Two pieces of banded graphene and one SWNT constitute a sandwich structure. Banded graphenes are arrayed face to face at a distance of 6.78 nm, clamping the left end of the SWNT. The SWNT is 6.1 nm in diameter with the chirality (45, 45). Hence, the distance between each graphene and the SWNT is about 0.34 nm, which is the equilibrium separation between graphenes or CNTs. The nucleotide is stored in the SWNT. It is positioned on the axis of the SWNT and with a distance of 8.5 nm to the left end of the SWNT. We carried out a three-step simulation: first the relaxation process, then the extrusion process, and finally the injection process. In the first process, we fixed the graphene, and relaxed the SWNT and the nucleotide at a prescribed temperature.

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In the second process, two springs with an elastic constant of 2×10^4 kJ/(mol·nm) were used to clamp two graphenes moving to each other at a speed of 0.1 nm/ps. To extrude the SWNT, the graphenes were constrained to move only in the *y*-direction. After finishing the extrusion process, we held two pieces of graphene at their final positions, and let the SWNT collapse completely.

We carried out the molecular dynamics simulations using the software GROMACS (Berendsen *et al*., 1995; Lindahl *et al*., 2001). The force field of GROMOS-96 (van Gunsteren *et al*., 1996) was used to describe the interactions among nucleic acids. Carbon atoms interaction in the SWNT is described by the combinations of a Morse bond, a harmonic cosine angle, and a cosine torsional potential (Walther *et al*., 2001). The non-bonding interactions among atoms of DNA and SWNT are characterized by the Lenard-Jones potential with parameters determined by geometrical average (van der Spoel *et al*., 2005).

The simulation was executed in two cases, noted as Case 1 and Case 2. The temperature of SWNT was maintained at the ambient temperature (300 K), via the Berendsen method (Berendsen *et al*., 1984) in both cases, and that of the ssDNA was maintained at 0 and 300 K, respectively, in Case 1 and Case 2 in the relaxation process. After the relaxation process, we maintained the temperature in Case 2, and stopped doing so in Case 1. SWNT with a length of 24.5 nm was used in Case 1, while SWNTs with the length from 14.6 to 29.4 nm were used in Case 2. The time step of 1 fs was used in all simulations.

3 Results and discussion

3.1 Mechanism of the injection

It has been proved that a nanotube with a large diameter would be stable at collapsed configuration (Gao *et al*., 1998; Tang *et al*., 2005). The section of the SWNT in a collapsed state resembles a dumbbell. The contacting zone of the SWNT is the dumbbell handle, while the tube-like parts at the two ends resemble the dumbbell ends.

Figs. 2a and 2b show the top views of the configuration of SWNT suffering collapse. We found that the contact zone (denoted by green atoms) has two different shapes: Shape 1—the head of the collapse wave is unbent in Fig. 2a; Shape 2—the head of the collapse wave is a segment of circle in Fig. 2b. These two shapes emerge in turn. When the contacting zone is in Shape 1, the head pushes the molecule in the SWNT move along the axis of the SWNT. Shape 2 provides the molecule a force component vertical to the axis, leading the molecule to change its moving direction toward the flank of the SWNT. Fig. 2c is the view from the outlet of the SWNT. The green atoms denoting the end of SWNT present an ellipse with large eccentricity. The area of the ellipse outlet is much smaller, and the two flanks are much closer, than for a circle. This provides opportunities for the nucleotide to adhere to the flank of the SWNT at the outlet. Then the nucleotide is inbreathed back into the tube-like part by the van der Waals interactions between the nucleotide and the SWNT (Gao *et al.*, 2003). This makes it more difficult for a nucleotide to exit the SWNT.

The different initial temperatures of the nucleotide lead to different vibration amplitudes. At a temperature of 0 K (Case 1), the nucleotide nearly holds still among the SWNT, while at 300 K (Case 2), it fluctuates due to the thermal vibration. Figs. 3a and 3b illustrate the positions and velocities in the *x*-direction for Case 1 and Case 2. The larger vibration amplitude drives the nucleotide away from the center of the SWNT. If the contacting zone emerges as a semicircle at the head of collapse wave, the molecule is pushed toward one of the two flanks of the SWNT, leading to the eventual inbreath of the nucleotide and failure of the injection. If the flat front shape of Case 1 prevails, the nucleotide is pushed out uniformly, and there is a greater probability of injection.

3.2 DNA injection by a modified carbon nanotube

Controlling the temperature of the nucleotide at 0 K would improve the probability of injection, though it was difficult to maintain the temperature of molecule in SWNT at 0 K in the experiment. Some advanced techniques produce defects on the wall of SWNTs (Sitharaman *et al*., 2005), and these defects can be labeled by an electrochemical method (Fan *et al*., 2005). Based on these techniques, one may envisage a modification to an SWNT (Fig. 4a). We produce two linear defects on both flanks of the SWNT at the outlet end. The defects length is about 4 nm. The collapse configuration of the SWNT with defects is quite different from that of the perfect SWNT, especially for the outlet shape. Green atoms in Fig. 4b indicate the outlet shape of the SWNT with defects suffering collapse. The yellow ellipse denotes the collapse mode of a perfect SWNT. Comparing these two modes, the outlet with defects is closer to a circle, and the distance between two flanks of the SWNT is larger. These characteristics make it more difficult for the nucleotide to adhere to the flanks, resulting in a higher probability of injection.

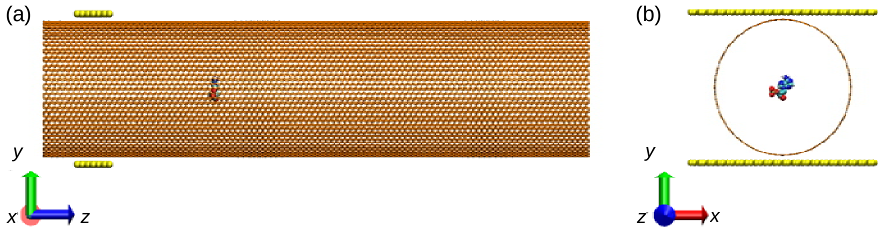


Fig. 1 Front view (a) and side view (b) of the simulation system

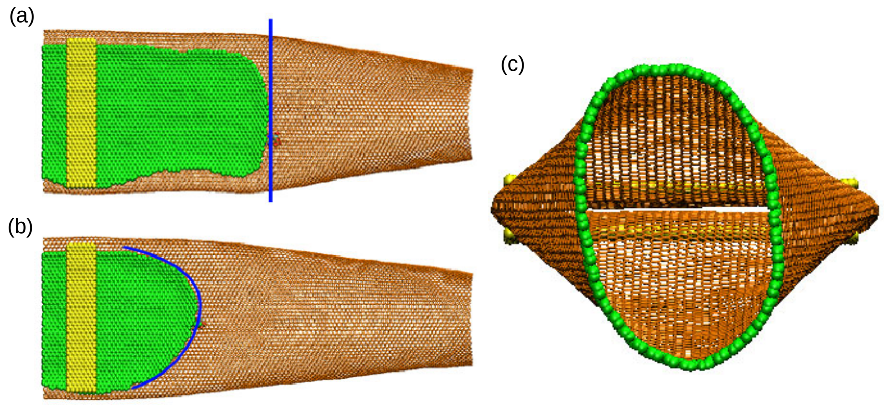


Fig. 2 Configuration of SWNT in a collapsed state
(a) and (b) are the top views of the configuration of SWNT suffering collapse with two different shapes; (c) View from the outlet of the SWNT

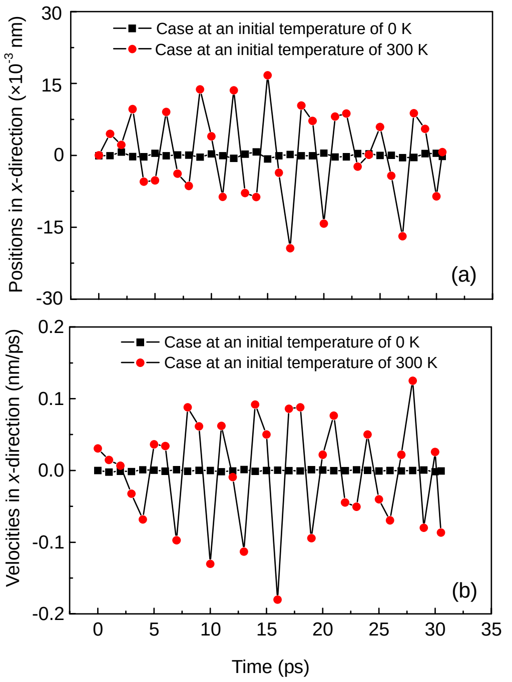


Fig. 3 Positions (a) and velocities (b) in the *x*-direction vary with time

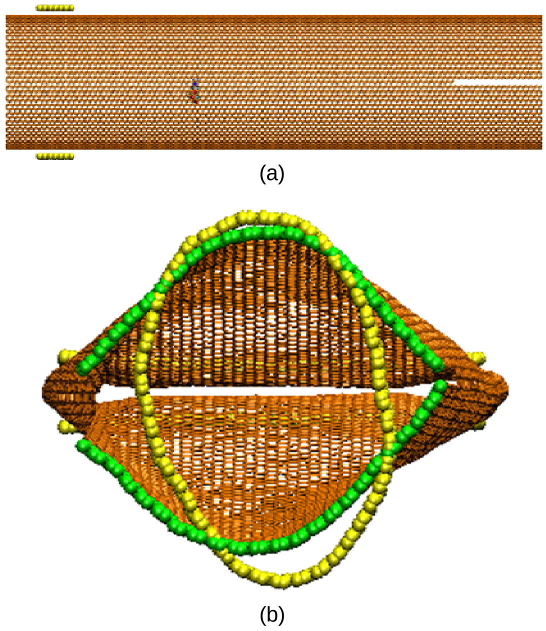
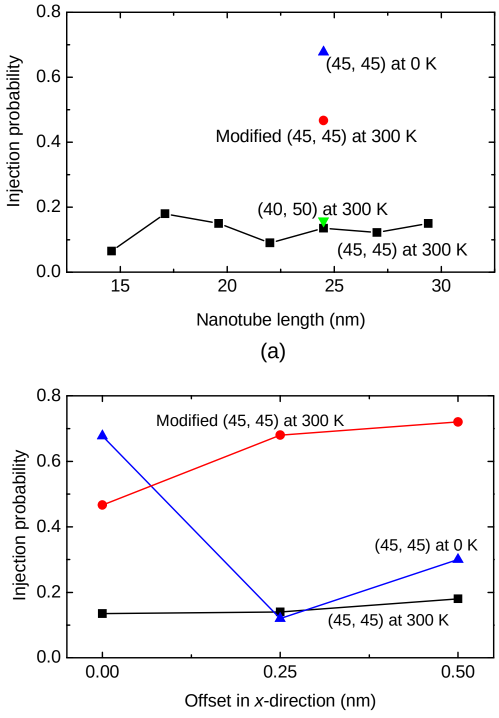


Fig. 4 Configuration of a modified SWNT nanogun (a) and the comparison for the outlet shapes between a perfect and a modified SWNT after collapse (b)

3.3 Probability of injection under different conditions

To investigate the influence of tube length on the injection probability, simulations of the SWNT with different lengths were carried out at an initial temperature of 300 K. We simulated 200 examples of each SWNT with different lengths from 14.6 to 29.4 nm. The probabilities of injecting the nucleotide out successfully at different lengths are shown in Fig. 5a as squares. All probabilities at different lengths are from 0.05 to 0.2, showing the lack of effect of tube length. Whatever the SWNT length, the nucleotide encounters similar outlet configurations at the end of the collapse process, and the nucleotide always adheres to the flank of the SWNT near the outlet due to the small distance between two flanks. The results for an SWNT with length of 24.5 nm at an initial temperature of 0 K is also drawn in Fig. 5a by triangle, while the modified SWNT is drawn with a circle. The latter two SWNTs have a higher probability of injecting the nucleotide. To investigate the influence of chirality on the injection probability, we took the (40, 50) SWNT, which has a similar radius to the (45, 45) SWNT. The probability is drawn as the upset-down triangle in Fig. 5a. The closeness of the results of (45, 45) and (40, 50) SWNTs at an initial temperature of 300 K indicates that the chirality bears little influence to the injection process.



(a)

(b)

Fig. 5 Probabilities of injection under different conditions
(a) Influence by structure of SWNT and the initial temperature of nucleotide. Squares (each data is furnished by 200 examples) denote the perfect SWNTs with different lengths at an initial temperature of 300 K; the circle (furnished by 30 examples) denotes the modified SWNT at an initial temperature of 300 K; the triangle (furnished by 30 examples) denotes the perfect SWNT at an initial temperature of 0 K, and the upset-down triangle (furnished by 96 examples) denotes the SWNT with the (40, 50) chirality at an initial temperature of 300 K. (b) Influence from nucleotide initial position offsets (furnished by 50 examples in each offset case) in the *x*-direction. Squares denote the (45, 45) SWNT at 300 K, triangles the (45, 45) SWNT at 0 K, and circles the modified (45, 45) SWNT at 300 K

The initial position of the nucleotide in the *x*-direction, on the other hand, bears influence to the injection probability. Simulations on different initial offsets of nucleotide in *x*-direction were carried out for a perfect SWNT in Case 2 (initial nucleotide temperature of 300 K) and Case 1 (initial nucleotide temperature of 0 K), as well as for a modified SWNT in Case 2. The influence is quite significant for the perfect SWNT in Case 1 (Fig. 5b). It hardly affects the perfect SWNT in Case 2, since the thermal fluctuation of the nucleotide blurs the role of the initial offset. The modified SWNT has certain robustness against the change in the nucleotide initial offsets, as shown in the curve with circles.

4 Conclusions

Molecular dynamics simulation indicates that an SWNT with a large radius has potential for a nano-injector of the nucleotide. The domino process takes place by compressing one end of the SWNT. The wave front drives the stored nucleotide to move. A percentage of the nucleotide will be injected out of the SWNT, while others will be inbreathed back into the SWNT. The injection probability depends on the initial temperature and initial position of the nucleotide, but not on the length of SWNT. Modification to SWNT has many advantages: it raises the injection probability at room temperature and has great robustness against changes in the initial nucleotide position.

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