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Molecular simulations on separation of atoms with carbon nanotubes in torsion

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ABSTRACT

Partition of noble atoms is studied using a pre-twisted single-walled carbon nanotube with semi-capped end via molecular dynamic simulations. A small portion on one end of the carbon nanotube is initially twisted to form a torsion buckling state. Upon releasing the pre-twisted portion, the collapse propagates along the tube wall. The van der Waals force between the encapsulated atoms and the collapsed wall of the nanotube thus initiates a motion and a consequent separation of the atoms. A successful separation of different atoms is found to be owing to the difference in the inertia of the atoms and the barrier effect of the semi-capped tip of the nanotube. Motions of one neon atom and one xenon atom are simulated to illustrate the separation process and various effects, such as twist angle and semi-capped tip, on the effectiveness of the process are discussed. Separation of eight atoms, four neon and four xenon, is demonstrated to further show the practical potential of the proposed partition method.

1. Introduction

The separation of gases has a wide range of applications in the clean energy, medicine, and chemical industries including ammonia purge gas, air dehumidification, helium recovery, nitrogen generation, hydrogen recovery, water purification and blood detoxification [1,2]. Recently, separating atoms and molecules using nano-materials, such as porous graphene [3–5] and carbon nanotubes (CNTs) [6], has drawn much attention.

Defect-free graphene is impermeable to atoms but can be made selectively permeable with the introduction of precise pores [3]. Thus, theoretical works on porous graphene membranes have been published mostly focusing on doping pores and controlling pore size and shape for gas separation [3–5]. Jiang et al. [3] studied the permeability of porous graphene membranes for separating hydrogen and methane mixtures by using molecular dynamics (MD) simulations. An electron beam from a transmission electron microscope [7] and heavy ion bombardment [8] were used to punch pores in graphene sheets. However, controlling the precise size and shape of pores as well as decorating pores still remain a challenge among researchers.

The potential of CNTs in transporting atoms and molecules, due to their hollow tube, large surface area and smooth walls, has been found to be efficient in various applications including drug delivery [9], nanopumping devices [10], nano-assembly, and spot-welding [11]. Recently, Wang [12] introduced a transportation of helium atoms with CNTs subjected to a torsion with a certain rate via MD simulations. When torsion applied to a CNT is beyond a critical value, the tube wall undergoes a collapsed state and formation of kinks, and hence experiences a propagation of the kinks along the tube. The propagation of the kinks, or local buckling state of the tube wall, becomes a driving force for moving atoms inside CNTs [12,13]. In practice, a twist as high as 180° was applied to a (14, 12) CNT by applying an electrostatic torque to the metal block suspended on the CNT [14]. Transportation of water molecules inside a CNT based on an energy pump, defined as a small pre-twisted portion of a CNT, was realized using MD simulations [15]. Similarly, the feasibility of ejection of DNA molecules from CNTs subjected to torsion was studied with MD simulations [16]. In addition, Wang [6] studied the possibility of separating encapsulated helium and carbon atoms with CNTs in torsion using MD simulations. It was concluded that a complete separation of atoms with CNTs make them good competitors for conventional membrane filters. Moreover, it was shown that the torsion rate and torsion angle can be adjusted to enable separations of different species of atoms using CNTs [6]. In the above work, the torsional rate applied to CNTs is found to be a critical factor in realizing a successful separation of atoms. However, it is impractical to control the rate and a feasible method for an efficient separation process is indispensable.

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In this work, we report a separation of xenon (Xe) and neon (Ne) atoms encapsulated in CNTs by using the pump concept via MD simulations for possible designs of filtration devices. The feasibility of separating two noble atoms, one Xe and one Ne, by means of an initially twisted CNT is studied. The appropriate range of pre-twist angle for the successful separation of Xe and Ne is obtained and various effects in the process are discussed. Last, partition of four Xe and four Ne atoms is elucidated to study the efficiency of the proposed separation mechanism.

2. Methods

Separation of noble atoms is studied with MD simulations, in which the trajectories of atoms and molecules are determined by numerically solving the Newton equations of motion for a system of interacting particles. Before each dynamic process, MD simulations involve a geometry optimization process, which refines the geometry of a structure with an iterative process until the potential energy of the structure is minimized. The dynamic simulations are conducted using NVT, a constant volume and constant temperature canonical ensemble, to allow the system to exchange heat with the environment. The interaction potential used herein is described by the universal force field (UFF), in which the force field parameters are estimated using general rules based on the element, its hybridization, and its connectivity [17]. In the UFF, the potential energy of an arbitrary geometry of a molecule is provided as a superposition of various two-body, three-body, and four-body interactions. The total potential energy E is expressed as [17]

$$E = R_R + E_\theta + E_\phi + E_\omega + E_{vdW} + E_{el} \quad (1)$$

where R_R, E_θ, E_ϕ, and E_ω are valence terms of bond stretching, bond angle bending, dihedral angle torsion, and inversion energies, respectively. E_{vdW} and E_{el} are nonbonding terms of van der Waals (vdW) and electrostatic energies. All dynamic simulations are carried out with time step of 0.5 fs to efficiently describe the dynamics process.

3. Separation of Ne and Xe atoms

The process of separating two noble atoms, Ne and Xe, is illustrated in details. The purpose of the separation process is to finally eject the lighter Ne atom outside of the tube, while the heavier Xe atom remaining inside the CNT. A 19 nm long (10,10) armchair single-walled CNT (SWCNT) with a semi-capped end is used for the preceding simulations at room temperature (298 k). A torsion angle of 90° is applied to the restrained pump portion with a length of 3.4 nm, marked by two red rings of carbon atoms shown by "A" and "B" in Fig. 1a, to initiate a local buckling state in the pump. Fig. 1a illustrates the initial configuration of the CNT, pre-twisted 90° in the pump portion, and the encapsulated Xe and Ne atoms after the geometry optimization process. Restraining atoms on a CNT can be practically carried out by preventing their freedoms in motion. In experiments, the restraints can be realized via the techniques of fixing atoms of a CNT such as forming an intramolecular junction as a restraint point described in [18]. Previous studies [15,16] have shown that removing the restraint on the pump part cause the collapsed wall, or kinks, propagate forward. The vdW force between the encapsulated atoms and the collapsed wall of the nanotube forms the driving force to push forward the atoms inside the CNT. Before the releasing process, the CNT is subjected to the NVT dynamic process with Anderson thermostat [19] for 50 ps at 298 K to reach a thermodynamic equilibrium. After removing the constraint on the right end of the pump, marked by "B" in Fig. 1a, the NVT dynamic process is conducted via Nosé-Hoover [20] thermostat for 12 ps at 298 K. Fig. 2 shows the axial velocities of Ne and Xe for the whole separation process, i.e. from 0 ps to 12 ps. Upon unlocking the restraint on the pump at $t = 0$ ps, the kinks propagate forward and motions on Ne and Xe are initiated at $t = 0.75$ ps, followed by a small period of interaction between the collapsed wall of the CNT and two atoms. Owing to the impact from the kinks, Ne and Xe are accelerated from rest to velocities of 3167 m/s during $t = 0.75$–1.25 ps and 1812 m/s during $t = 0.75$–2 ps, respectively. It is seen that Ne atom is easier to be accelerated to a higher initial velocity than Xe, in a shorter time, by the impact of propagating kinks, since the mass of Ne is smaller than that of Xe. Fig. 1b shows the snapshot of the separation process at $t = 1.75$ ps, in which Ne has already entered the 12.3 nm long grey-colored channel portion. Note that outset of the channel portion is the stopper, marked by "C" in Fig. 1a, which is a ring of carbon atoms fixed right after encapsulated atoms to prevent propagation of the kinks to the channel portion. Without the stopper, the collapsed wall of CNT propagates faster than moving atoms and would block the motion of them, as observed from our simulations.

The fluctuation of Ne and Xe axial velocities is clearly observed in Fig. 2, which can be attributed to the method of controlling the system temperature during simulations, i.e. Nosé–Hoover thermostat, and also crystalline structure of the CNT wall, i.e. periodic rings along axial direction of the CNT. Moreover, it is seen from Fig. 2 that the average axial velocities of Ne during $t = 1.25$–3.25 ps and those of Xe during $t = 2$–4 ps decrease slowly after entering the channel portion, but become constants afterwards. The reason behind this observation is that Ne and Xe encounter high fluctuations after entering the channel, resulting in high friction between encapsulated atoms and the channel. However, the decreased constant average velocities of Ne and Xe are observed 2 ps after their entering the channel due to the decrease of fluctuations in motions, and consequently the reduction of the friction between atoms and the channel. The average axial velocities of Ne and Xe after the high fluctuation period in the channel are 2361 m/s and 1365 m/s, respectively.

Ne and Xe reach the end of the channel at $t = 6.25$ ps and $t = 10$ ps, respectively, with axial velocities of 2618 m/s and 1466 m/s, as shown in Fig. 2. The passing of Ne atom through the semi-capped end is readily recognized in Fig. 2 with a sharp velocity drop to 869 m/s during the interval $t = 6.25$–6.75 ps, followed by a velocity increase up to 1645 m/s at $t = 7.25$ ps. These behaviors are results of the tip barrier or template effect [21] owing to the strong vdW force between the encapsulating atom and the semi-capped tip that prevents the ejection of the atom. The repulsive vdW force between Ne and the semi-capped end causes Ne to speed up after exiting the CNT. Fig. 1c exhibits the snapshot of the process at $t = 7.25$ ps, in which Ne atom has successfully been ejected from the tube. Fig. 2 indicates that the axial velocity of Xe atom decreases from 1466 m/s to −964 m/s during the period $t = 10$–11 ps, implying that Xe has been repelled by the end barrier. The snapshot of the favored separation at $t = 11.75$ ps is provided in Fig. 1d, in which Xe atom is moving to the left with an axial velocity of 967 m/s after being prevented by the CNT semi-capped tip. Upon continuation of the dynamic process, it is observed that Xe atom continues moving back and forth along the channel without exiting the CNT. The reason of these observations is that the velocity of Xe atom is not high enough, unlike Ne, to pass through the tip of the CNT by overcoming the template effect. For further elaboration, the video of the whole process is provided in Supporting information 1. It is worth mentioning that the cap of a pristine CNT can be modified to semi-capped by electrical and physical treatments as follows. Tip of a CNT can be modified precisely through controlled field emission process [22] and field evaporation process [23]. Moreover, carbon atoms can be locally vaporized