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Formation of carbon nanoscrolls from graphene nanoribbons: A molecular dynamics study

Y. Wang [a], H.F. Zhan [b], C. Yang [a], Y. Xiang [a], Y.Y. Zhang [a,*]

[a] School of Computing, Engineering and Mathematics, University of Western Sydney, Locked Bag 1797, Penrith, NSW 2751, Australia
[b] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, 2 George St, Brisbane, QLD 4001, Australia

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ABSTRACT

Carbon nanoscrolls (CNSs) are one of the carbon-based nanomaterials similar to carbon nanotubes (CNTs) but are not widely studied in spite of their great potential applications. Their practical applications are hindered by the challenging fabrication of the CNSs. A physical approach has been proposed recently to fabricate the CNS by rolling up a monolayer graphene nanoribbon (GNR) around a CNT driven by the interaction energy between them. In this study, we perform extensive molecular dynamics (MD) simulations to investigate the various factors that impact the formation of the CNS from GNR. Our simulation results show that the formation of the CNS is sensitive to the length of the CNT and temperature. When the GNR is functionalized with hydrogen, the formation of the CNS is determined by the density and distribution of the hydrogen atoms. Graphyne, the allotrope of graphene, is inferior to graphene in the formation of the CNS due to the weaker bonds and the associated smaller atom density. The mechanism behind the rolling of GNR into CNS lies in the balance between the GNR–CNT van der Waals (vdW) interactions and the strain energy of GNR. The present work reveals new important insights and provides useful guidelines for the fabrication of the CNS.

1. Introduction

Recently a new form of carbon-based nanomaterials, carbon nanoscroll (CNS) has attracted extensive research interests. A CNS can be regarded as a monolayer graphene nanoribbon (GNR) rolling up in a spiral form with a structure similar to a multi-walled carbon nanotube (MWCNT). Unlike the closed carbon nanotubes (CNTs), CNS is topologically open-ended, like a Swiss roll as depicted in Fig. 1. Owing to its unique structure, CNS possesses some interesting properties which could lead to different potential applications.

The CNSs were first discovered by Bacon in 1960 [1]. In recent years, extensive investigations have been carried out to explore their fundamental properties, such as mechanical [2–7], electronic [3,8–10] and optical properties [11]. It has been reported that CNSs have various appealing applications [12–21]. For example, Mpourmpakis et al. [13] demonstrated that an opening of the CNSs' spiral structure to 7 Å followed by alkali doping can enhance their hydrogen storage capacity up to 3 wt%. Shi et al. [16] found that a substrate-supported CNS can be controlled to roll forwards and backwards by tuning its interlayer interaction energy via an external electric field, indicating its promising applications as actuators and motors in nanomechanical systems. Cheng et al. [18] investigated a CNS oscillator, which can oscillate around an equilibrium configuration at frequencies on the order of 10 GHz by modulating the CNS's effective surface energy. It is evident from the findings of Shi et al. [20] that CNS is better than CNT in the application of tunable water channel due to its larger water permeability and sensitivity.

Attempts have thus been made to fabricate the CNS chemically and physically [21–35]. CNS was first synthesized via a chemical approach in which the graphite was intercalated by alkali metals, exfoliated with ethanol and sonicated. The resulting graphite then can roll into scrolls with undetermined number of layers [22]. A recent experimental work has shown that CNS can be rolled up from the SiO_2-supported monolayer graphene immersed in isopropyl alcohol (IPA) solution [26]. In general, the chemical approach for the fabrication of CNS fails to produce perfect CNS without defects, control the rolling direction and the layer number. To overcome the limitation of the chemical approach, a physical approach has been proposed, in which a monolayer GNR can be rolled up to form a CNS by using a CNT as the initiator [31–33]. In this method, a CNT is firstly placed in close proximity to a GNR. Owing to the van der Waals (vdW) interaction between CNT and GNR, the GNR is forced to deform and roll around the CNT surface and eventually

* Corresponding author. Tel.: +61 2 47360606; fax: +61 2 47360833.
E-mail address: yingyan.zhang@uws.edu.au (Y.Y. Zhang).

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forms a CNS. Researchers showed that the formation of the CNSs in this way is dependent on the CNT diameter [32,33], the initial position of the CNT relative to the GNR [33], and the chirality of the CNT and GNR [33]. Besides, it was reported that this method is more efficient in vacuum than the GNR being placed on a substrate, because in vacuum no energy is required to overcome the interaction between the GNR and the substrate [31,32]. Perim et al. [32] have proved that using the substrate with chambers/pits is able to remove the effect of the substrate effectively on the formation of CNSs.

In this work, we further explore the formation of the CNSs by accounting for other important factors, such as the length of CNTs, functional groups in GNR and temperature by using molecular dynamics (MD) simulations. The possibility of the graphynes, the graphene allotropes, in the fabrication of CNS is also investigated.

2. Molecular dynamics simulation methods

The simulation model consists of a CNT and a GNR as shown in Fig. 2. The length of the CNT is equal to the width of the GNR. Unless otherwise stated, the (10,10) SWCNT is used in the simulations while the dimension of the GNR $L \times W$ is, $\sim 480 \times 80$ Å^2 with a zigzag direction along its length direction. Initially, the CNT is placed at a distance of 10 Å away from one edge of the GNR. In the z-direction, the CNT is 3.4 Å above the GNR, which is the equilibrium distance between the CNT and GNR. The bonded interaction between carbon atoms is described by the reactive-empirical bond order (REBO) potential [36], which has been widely used in the simulation of carbon-based materials. Prior to the simulation, the initial equilibrium models were achieved by the conjugate gradient method. Thereafter, the system was relaxed in a canonical (NVT) ensemble (i.e. constant atom, volume and temperature) with a time step of 1 fs. During the simulations, Nose–Hoover thermostat was used and the temperature was kept 300 K unless otherwise stated. Each simulation was run up to 0.5 ns. All the simulations were performed in LAMMPS [37] under the identical conditions unless otherwise stated.

3. Results and discussion

The formation of CNS is driven by vdW interaction and it is accompanied by the elastic deformation of the GNR. The CNS can be formed if the interaction energy between CNT and GNR can overcome the required deformation energy of GNR.

3.1. Geometric effect from dimensions of CNTs

Firstly, the effect of the CNT length on the formation of CNS is analyzed. A series of simulations of 480×80 Å^2 GNR interacting with (10,10) SWCNTs of different lengths are performed. The SWCNTs with eight different lengths in the range of 20 Å and

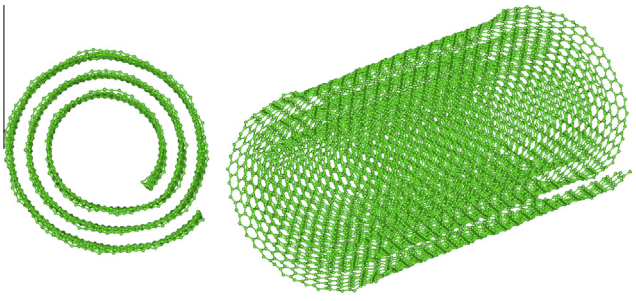

Fig. 1. Side and perspective view of a three-walled CNS.

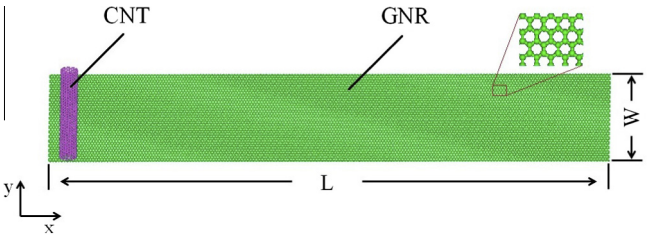

Fig. 2. Simulation model of a GNR (green) and a SWCNT (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

160 Å are considered. The results show that the CNTs with a length larger than 50 Å are able to initiate the rolling of this 80 Å-wide GNR into a CNS. When the CNT length is smaller than 50 Å, no CNS can be formed. Fig. 3 depicts the snapshots of the GNR interacting with a 50 Å and 40 Å-long SWCNT. With the aid of the 50 Å-long SWCNT, the GNR completely rolls into a CNS at $t = 125$ ps. Before $t = 125$ ps, the average potential energy (in unit of eV/atom) in the system keeps increasing as shown in Fig. 3(a). This can be explained as below. During the rolling procedure, the GNRs experience bending deformation and roll into a multiple-layer CNS (the number of the layers in CNS depends on the length of the GNR provided that the diameter of CNT is fixed). The deformation of GNR and the interlayer interactions lead to the increasing of the elastic strain energy and the non-bonded vdW potential energies, respectively. Thus the potential energy of the system is increased. When the rolling procedure finishes, the average potential energy fluctuates around −7.34 eV/atom, indicating that the system is energetically stable without significant geometry deformation. On the other hand, the 40 Å-long CNT is able to initiate a slight deformation at the end of the GNR, but it fails to activate the rolling of the GNR into a CNS. This phenomenon can be understood from the perspective that the vdW interaction between the GNR and the CNT at the beginning depends on the interaction area. The vdW force is smaller for a shorter CNT, which is too weak to overcome the elastic deformation of GNR over the rolling process. In this case, the average potential energy in the system remains almost unchanged during the whole simulation duration as shown in Fig. 3(f). The average interaction energy between CNT and GNR is −0.0030 and −0.0033 eV/atom for the 40 Å-long CNT and 50 Å-long CNT, respectively. The smaller interaction energy in the former case is unable to drive the formation of the CNS.

3.2. Effect of temperature

To investigate the effect of temperature on the formation of CNSs, the interaction between a 480×80 Å^2 GNR and an 80 Å-long (10,10) SWCNT under different temperatures varying from 0.1 K to 300 K was simulated. It was found from the simulation results that the GNR can wrap the CNT as long as the temperature is higher than 1 K. Below 0.5 K, the GNRs deform at their ends, but fail to roll into CNSs as illustrated in Fig. 4. This phenomenon agrees well with the findings in the previous works [38,39]. The reason is there exists an energy barrier during the transformation from GNR to CNS. At an extremely low temperature, the GNR atoms have no enough thermal energy to overcome the initial energy barrier for bending. In this model, as the temperature is increased to 1 K or higher, the thermal energy increases significantly which could overcome the energy barrier and thus triggers the formation of CNS as observed in Fig. 4. The temperature during the simulation was found to fluctuate within 1% of the set values, indicating that the effect of temperature is well described by the Nose–Hoover thermostat.