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Defect-induced carbon nanoscroll formation

Joseph Wallace, Lin Shao *

Department of Nuclear Engineering, Texas A&M University, College Station, TX 77843, USA

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ABSTRACT

Carbon nanoscrolls (CNSs), a graphitic structure formed by rolling of a graphene plane, must overcome an energy barrier in order to form. This energy barrier is the result of competing interactions between the van der Waals force, which wants to cause overlap of the graphene, and the torsional or bending force, which resists bending of the graphene plane. In this study we used molecular dynamics simulation to examine the effect of vacancies on the CNS formation dynamics. We found that the energy barrier, which must be overcome to obtain a stable scroll structure, can be lowered or completely eliminated by introducing vacancies. Individual vacancy and divacancy configurations are studied and found to reduce the torsional bending energy by allowing local stress relaxation around the defect site. A structural transition diagram is created in which we show the energy barrier height for a range of vacancy concentrations and CNS rolling widths. These results provide the theoretical backing for a new method of fabricating CNSs using a focused ion beam and shed new light on the self-rolling phenomenon in graphene.

1. Introduction

Graphitic systems, including graphene, carbon nanotubes (CNTs) and fullerenes have been at the forefront of nanotechnology since the field's inception in the mid-1980s. With the discovery of each of these graphitic systems intensive research ultimately led to a number of potential technological applications [1–3]. Another promising graphitic system that has received significantly less attention is carbon nanoscrolls (CNSs). Similar in some ways to multiwalled carbon nanotubes, a CNS is formed by rolling up a sheet of graphene creating a tube-like structure. CNSs are expected to share a number of properties with other graphitic systems such as high mechanical strength, high thermal conductivity and high electrical conductivity [4–7]. In contrast, the novel topology in CNSs exposes a number of unique properties. For example, electron transport in CNSs occurs throughout the entire system as opposed to MWCNT structures in which the current is confined to each layer. Additionally, CNSs will more easily accept intercalation of compounds due to the open structure as opposed to CNTs which will strongly resist lattice expansion [8,9]. These properties have led to a number of proposed applications including hydrogen storage [8], super capacitors [10] and nanoactuators [11–14].

Despite these promising applications, how to fabricate these structures controllably remains a great challenge. Carbon nanoscrolls were first produced by the arc discharge method by Bacon in 1960 [15]. Synthesis methods have since greatly improved. One method for synthesizing carbon nanoscrolls involves the use of an isopropyl alcohol solution to rollup graphene on SiO_2/Si wafers [14]. Other methods include sonochemical [16] and ultrasonication [9]. Braga et al. used molecular dynamics simulation to show that the formation and stability of CNSs results from a competing interaction between the torsional or bending force which wants the graphene to lay flat, and the van der Waals force which pulls the

* *Corresponding author:* Fax: +1 9798456443.
E-mail address: lshao@tamu.edu (L. Shao).
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layers together [17]. Furthermore, Braga et al. showed that these competing interactions result in a potential energy barrier which can be overcome by bending the graphene layer to the point of overlap. Regardless of synthesis method, this potential energy barrier must be overcome to form a CNS.

Herein we report the first results that show local structural relaxation via vacancy introduction can significantly lower the potential energy barrier. Beyond a certain vacancy concentration, the potential energy barrier is completely removed, meaning the sheet could roll up without the need for external energy. A number of CNS systems of varying width and vacancy concentration are modeled such that a map of stability as a function of two controllable parameters, dimensions and defect numbers, could be created.

2. Modeling

The classical molecular dynamics code, LAMMPS, [18] along with the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) [19] potential were used to model the CNS systems. The AIREBO potential is capable of describing graphene systems by including bond stretching, bond angles, dihedral angles, van der Waals force, and electrostatic forces. All CNS systems were created by rolling a sheet of graphene into a truncated archimedean spiral [20] such that the interatomic bond spacing is maintained constant. Fig. 1a shows the flat plane of graphene in which the width is defined to be perpendicular to the rolling axis and the length is defined to be parallel. We define the inner radius to be the distance from the center of the CNS to the inner most atomic row as indicated by the red arrow in Fig. 1b. The interplanar spacing in all CNS systems is 3.354 Å, which agrees well with experimentally determined interplanar spacing of 3.5 [14]. For sake of simplicity, all CNS systems considered have zigzag chirality.

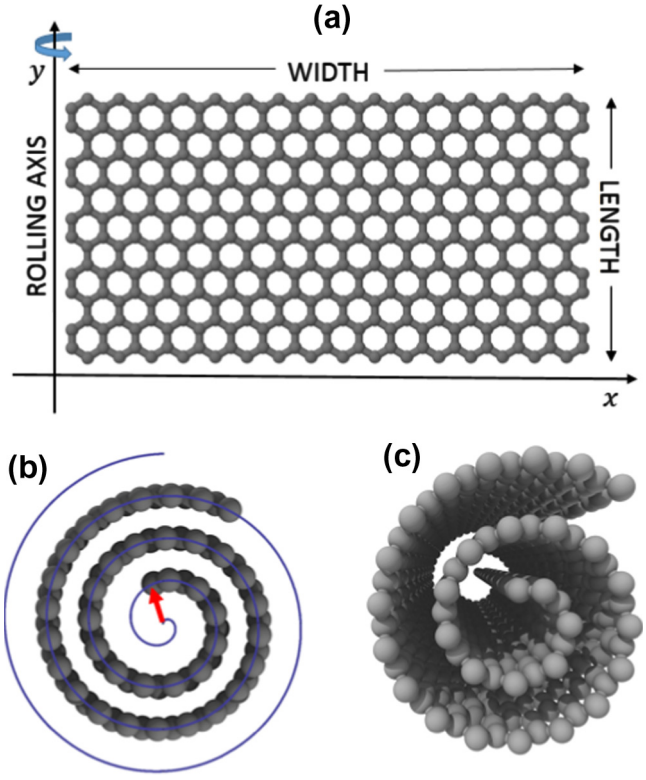

Fig. 1 – (a) Graphene plane showing the rolling axis with width defined perpendicular to the axis and length defined parallel, (b) carbon nanoscroll conforming to the shape of an Archimedean spiral [20] with the red arrow indicating the inner radius and (c) perspective view of the a CNS with width of 91.8 Å (same width used in the CNSs of Fig. 2). (A color version of this figure can be viewed online.)

Starting from a flat plane of graphene, 0.25% of carbon atoms are randomly removed, which accurately simulates the vacancy creation process upon particle irradiation. Under particle irradiation from electrons, light ions, and high energy heavy ions, damage cascade creation is less likely due to the relatively small nuclear stopping power compared to the electronic stopping power [21]. Thus, the defect creation is dominated by point defects. In addition, the ease of sputtering atoms from graphene suggests vacancies are the dominant point defect type [22,23]. Therefore, randomly introducing vacancies represents the defect morphology likely created in practical ion irradiation conditions. After defect loading, the system is annealed at 3000 K for 40 ps. The high temperature annealing provides a means for quickly reaching stable defect configurations expected in an experiment. This defect loading and relaxation process is repeated until the desired vacancy concentration is obtained. Next, the defective graphene sheet is rolled into a CNS with the desired inner radius. Then, the edge atoms are fixed in place while all other atoms are allowed to evolve in time at a temperature of 0.15 K with a timestep of 0.1 fs for 2 ps.

3. Results and discussion

Fig. 2a shows the per-mol change in potential energy relative to a flat plane of graphene for three vacancy concentrations in a CNS of width 91.8 Å and length of 418.8 Å. To allow for the comparison among the curves, each system's reference energy or zero energy was chosen as the energy of the system at infinite inner radius. It should be noted that the system energies increase with increasing defect levels, going from 2.51 Kcal/mol to 4.62 Kcal/mol (above the defect free level) for 1.5% and 5.0% defect levels respectively. We further compare the energies of different systems to check consistency. In a comparison with a defect-free graphene, the energy of defect-free bi-layer graphene is about 0.35 Kcal/mol below, and that of graphite is about 1.1 Kcal/mol below. As previously shown by Braga et al., the potential energy of the vacancy free CNS will initially increase due to the bending of the graphene plane. This energy increase arises due to the three and four body angle, dihedral angle and improper dihedral angles formed in the graphene plane. The change in energy due to the changing bond angles is described by the AIREBO potential. Once the graphene reaches a critical overlap, the van der Waals force takes over and a self-sustaining rollup process begins. The potential energy barrier is defined to be the energy difference between a flat plane of graphene and a CNS at the point of initial overlap. The potential energy barrier height for the vacancy free case is 0.112 Kcal/mol. Introducing 1.5% vacancy concentration lowers the barrier