Journal of Molecular Structure 1125 (2016) 282–287

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

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

Danhui Zhang [a, b, *], Houbo Yang [a]

[a] College of Mechanical Engineering, Linyi University, Linyi 276005, China
[b] Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, China

ARTICLE INFO

Article history:
Received 19 May 2016
Received in revised form
26 June 2016
Accepted 29 June 2016
Available online 1 July 2016

Keywords:
Graphehe
Carbon nanoscroll
Molecular dynamics
Carbon nanotubes

ABSTRACT

In recent year, carbon nanoscrolls have attracted intensive attention both in theory and experiments for their unique and excellent fundamental properties and the wide range of potential applications. In this paper, the fabrication of carbon nanoscrolls using graphene and carbon nanotubes has been studied by molecular dynamics (MD) method. The formation mechanism of carbon nanoscrolls has been presented convincing explanations. Furthermore, the position and number of carbon nanotubes also influence the formation of carbon nanoscrolls. Our theoretical results will provide researchers a powerful guide and helpful assistance in designing better targeted programs in experiments.

1. Introduction

Graphene(GN), a new two-dimensional thin film material and firstly exfoliated from the bulk graphite, has received intensive attention due to its unique electrical and mechanical properties [1]. With the development of nanotechnology, various experimental methods have been applied to fabricate graphene with desired geometry [2–4]. Besides, the physical and chemical properties of graphene can be easily controlled [5–7], which makes graphene a promising candidate for real applications such as nanoelectronic devices [8], biofunctional materials [9], solar cells [10] and sea water desalination [11].

Carbon nanotubes(CNTs), which are discovered in 1991, are also the most promising nanomaterials in the carbon family due to their ideal 1D structures. They have attracted tremendous interest because of their unique properties [12] and promising applications [13]. The properties of CNTs have been investigated in great detail during the past few years and research into GN is rapidly catching up with that of CNTs. Design and fabrication of functional carbon nanostructures is a challenging but meaningful mission for scientists to propel the development of nanotechnology, such as nanopharmacology, nanobiology and nanofluidic manipulation. In order to fabricate the carbon nanostructures, using forced-field-based molecular dynamics simulations, we proposed a feasible method to obtain the carbon nanostructures through self-scrolling of graphene flakes. Buehler et al. [14] has reported that graphene can be assembled into nanoscroll under high aspect ratio to minimize the surface energy. Some other rod-like materials such as iron nanowire, silicon nanowire, etc. can also activate the scrolling of graphene [15]. Experimentally, metal nanoparticle encapsulated by graphene has also been observed [16].

Here, by using molecular dynamics simulations, we investigate a simple method of synthesizing novel carbon nanotube/carbon nanoscolls core/shell-composite nanostructures by the rolling up of single graphene sheets induced by CNTs. Actually, the graphene-carbon nanotube composite was found to exhibit photoinduced electron transfer, which indicates that the composite can be a candidate for fabrication of all-carbon solar cells [17]. Furthermore, the effects of position and number of carbon nanotubes on the assembly will also be investigated in details.

2. Simulation method

In this work, all calculations were carried out by molecular dynamics (MD) simulation, and the atomic interaction was described by the force fleld of condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [18]. COMPASS

* Corresponding author. College of Mechanical Engineering, Linyi Univeristy, Linyi 276005, China.
E-mail address: njustzdh@126.com (D. Zhang).

http://dx.doi.org/10.1016/j.molstruc.2016.06.083
0022-2860/

is an ab initio force field that has been parametrized and validated using condensed-phase properties in addition to various ab initio calculations and experimental data, with a functional form that includes covalent terms as well as long-range, non-bond (van der Waals (vdW)) interactions and electrostatic forces. It aims to achieve high accuracy in prediction of the properties of very complex mixtures [19–22] and it has been proven to be applicable in describing the mechanical properties of graphene nanosheets(GNSs).

The force field was expressed as a sum of valence, cross-terms, and nonbonding interactions:

$$E_{\text{total}} = E_{valence} + E_{cross-term} + E_{nonbond}$$

$$E_{nonbond} = \sum_{i>j} \frac{q_i q_j}{r_{ij}} + \sum \ell_{ij} \left[2\left(\frac{r_0}{r_{ij}}\right)^9 - 3\left(\frac{r_0}{r_{ij}}\right)^6 \right]$$

The valence energy, $E_{valence}$ was generally associated with the terms including bond stretching, valence angle bending and dihedral angle torsion. The cross-term interacting energy, $E_{cross\text{-}term}$, accounted for the factors such as bond or angle distortions caused by nearby atoms to accurately reproduce the dynamic properties of molecules. The nonbonding interaction term, $E_{nonbond}$, accounted for the interactions between nonbonding atoms. Here, q was the atomic charge, r_{ij} was the i-j atomic separation distance, and ℓ_{ij} was the off-diagonal parameter. These parameters were fitted from quantum mechanics calculations and implemented into the Discover module of Materials Studio.

The MD simulations were performed in armchair GNS with size of 292.740 Å (arm-chair direction) × 71.34 Å(zigzag direction) and carbon nanotubes(8,8) with length 61.49 Å and diameter 10.85 Å. The dynamic process was conducted in NVT (the volume and the temperature were constant) ensemble at 298 K. The Andersen method [23,24] was employed in the thermostat to control the thermodynamic temperature and generate the correct statistical ensemble. The thermodynamic temperature was kept constant by allowing the simulated system to exchange energy with a "heat bath". The time step in MD simulation was 1 fs, and the data were collected every 2 ps. All the simulations were long enough to detect several cycles of thermal vibration, and the full-precision trajectory was recorded.

3. Results and discussion

3.1. The spontaneous scrolling of GNS

Direct simulation shown in Fig. 1 provides snapshots of the spontaneous scrolling of an armchair GNS onto a carbon nanotube(CNT). The GNS is placed vertically to the axis of CNT and the attractive force between them makes the GNS approach to the CNT rapidly. The GNS displays discontinuous wrinkles or corrugations in several nanometers thick (shown in Fig. 1), demonstrating its thermodynamic instability. According to the so-called Mer-min-Wagner theorem [25] that long-wavelength fluctuations destroy the long-range order of 2D crystals, these fluctuations can be suppressed by anharmonic coupling between bending and stretching modes, which presents that a 2D GNS can exist but exhibit strong fluctuations with some ripples and corrugations. After the GNS attaching onto the CNT, the GNS begins to curl and wrap around the CNT to form a coiling with a tail just like a tadpole (at t = 40 ps). When totally wraps the CNT, the GNS begins to scroll spontaneously. At t = 320 ps, it is found that the tadpole-like part starts to fold and slide with a lower speed. Eventually, the self-scrolling completes and the configuration of GNS transforms from

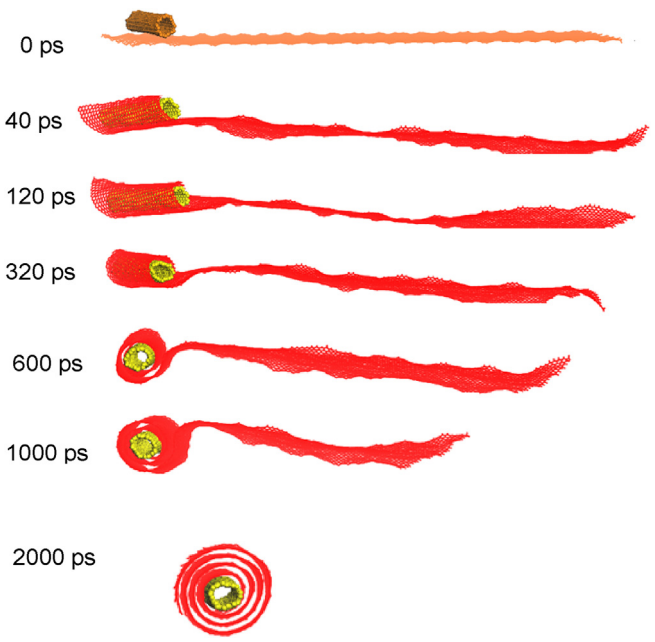

Fig. 1. Snapshots of the spontaneous self-scrolling of a GNS onto a CNT.

a planar membrane to a tubular scroll. During the self-scrolling, the speed is determined by the rate of releasing potential energy into the kinetic energy. Our simulation result indicates that the average self-scrolling speed of the GNS reaches up to 8.5 m/s. Furthermore, the CNT is also found to be deformed owing to the strong interaction between GNS and CNT during the self-scrolling process.

3.2. Interface characteristics

The interaction energy reflects the adhesion intensity between the GNS and the CNT which can be calculated from the following equation:

$$E_{\text{interaction}} = E_{\text{total}} - (E_{GNS} + E_{CNT})$$

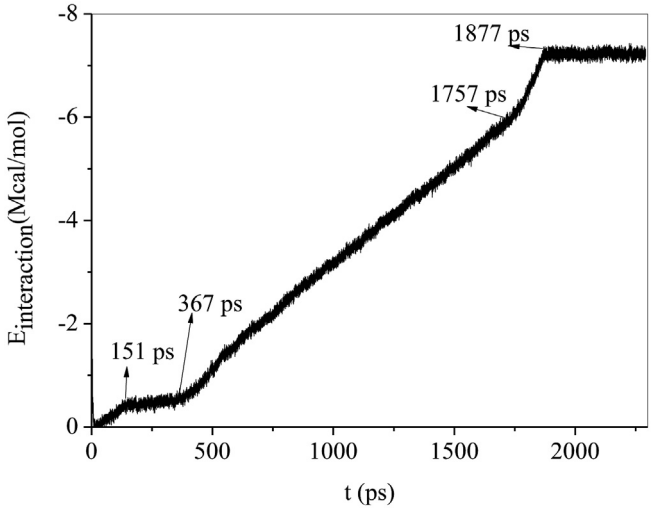

Fig. 2. The interaction energy between GNS and CNT with time.