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Self-assembly of graphene nanoribbon ring on metallic nanowires

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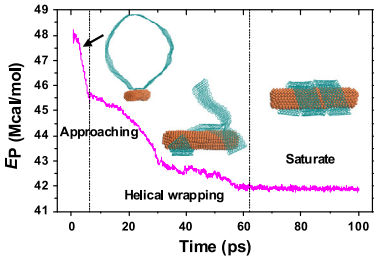
HIGHLIGHTS

- It demonstrates that metallic NW can activate and guide the self-assembly of GNR.
- GNR adopts bilayered helical configuration on NWs.
- Different geometrical factors of the GNRs are taken into calculation.
- This simple self-assembly provides a powerful way to fabricate various kinds of heterojunction nanomaterials of graphene.

GRAPHICAL ABSTRACT

Metallic nanowires can activate and guide the self-assembly of graphene nanoribbon rings, allowing them to adopt a bilayered helical configuration.



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ABSTRACT

Molecular dynamics simulations demonstrate that metallic nanowires (NWs) can activate and guide the self-assembly of graphene nanoribbon rings (GNR), allowing them to adopt a bilayered helical configuration on NWs. This unique technology attributes to the combined effects of the van der Waals force and the π–π stacking interaction. The size and chirality effects of GNR on the self-assembly of GNR–NW system are calculated. Diverse NWs, acting as an external force, can initiate the conformational change of the GNRs to form bilayered helical structures. The stability of the formed nanosystems is further analyzed for numerous possible applications.

1. Introduction

Increasingly, self-assembled systems have been widely studied because such materials may not only be designed to be highly dynamic, displaying adaptive and self-healing properties, but could also help gain an understanding of the rules that govern molecular assembly processes [1]. Graphene [2], a single-atomic sheet of carbon atoms arranged in a honeycomb lattice, has stimulated an unprecedented upsurge of research interest on the quantitative understanding of highly enriched physical and chemical properties of graphene and graphene-based materials, which have been widely explored for applications in many different fields [3–6]. Experimental and theoretical studies have validated that graphene tends to transform into a more compact structure to minimize its surface energy for stability [7]. The graphene flakes and nanoribbons with high flexibility can self-assemble into various three-dimensional nanostructures [8] and large constructions [9–11] due to strong interlayer van der Waals (vdW) coupling and chemical functionalization at their edges. Moreover, highly elastic graphene under the help of other materials such as carbon nanotubes (CNT) [12–14] and water [15] could self-assemble on them into helix [12,13], nanoscrolls [14–17] and a variety of other three-dimensional nanostructures [15].

Graphene nanoribbon rings (GNR) with circular structures are also indispensable for graphene-based device application, because its physical and chemical properties can be easily tuned by controlling ring width, layer number, edge configuration and orientation. Metallic nanowire (NW) is a one-dimensional nanostructure with electrical

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carriers confined in the other two perpendicular directions. NWs with magic structures exhibit interesting physical properties [18] that are noticeably different from those of quantum dots and the bulk. Of particular importance in technology is that NWs have potential applications in many fields such as optoelectronics, photovoltaic cells and especially device miniaturization [19–20]. New composite functional materials could be prepared if GNR nanostructures self-assemble onto the surfaces of one-dimensional NWs, which may extend many additional fascinating phenomena and make them promising candidates for applications in electronics and biomedicine. Thus, detailed analysis at an atomic level is starved for both qualitative and quantitative understanding of special GNR–NW self-assembled systems. It can provide guidance and supplement for experimental studies, which will spark a great effect on the synthesis of novel GNR–NW based functional nanomaterials and eventually on their applications into nanoscale devices.

Using molecular dynamics (MD) simulations, a simple model of self-assembling GNR to form bilayered-helix nanostructures on different NWs is investigated systematically. In this work, the surface attraction stress of NWs is used to guide and deform GNRs such that they roll up and adhere onto the outer surface of the NW by self-assembly. The self-assembled process consists of two basic steps: (1) GNRs approaching NWs and collapsing; (2) bending and rolling of GNRs into a bilayered helical conformation directed by the surface stress of NWs and the π–π stacking effect. This work provides a simple and energy-saving way to fabricate helical graphene composites in theory and some rules could be generalized from the obtained discovery to control this intriguing process as needed. In addition, the self-assembly behavior of GNR and metallic NW may trigger enormous interests in chemical functionalization and helical graphene synthesis, which are helpful for synthesizing novel helical graphene-NW based functional materials, and eventually be beneficial for fabricating nanoscale devices.

2. Methodology section

The self-assembly of GNR onto metallic NWs is simulated by the molecular dynamics (MD) method and the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force-field [21], an *ab initio* force-field that is parameterized and validated using condensed-phase properties in addition to various *ab initio* and empirical data, was applied to model the atomic interaction. It has been proven to be applicable and accurate in describing the interaction of carbon materials with various substances [22,23] including metals [24–26]. All the MD simulations described in this work were performed under the constant volume and constant temperature dynamics (NVT) ensemble. The Nose method in the thermostat was applied to control the temperature at 298 K and generate the correct statistical ensemble. All the simulations were conducted in vacuum without periodic boundary conditions so that there is no pressure coupling. The initial velocities of each atom followed a temperature-dependent Maxwell–Boltzmann distribution and the Verlet algorithm was adopted to integrate the motion of equations of the whole system. The interval of each MD simulation step was typically 1.0 fs. Here, the MD simulation for each case study was performed long enough to achieve an equilibrium state.

GNRs with different chirality, circumferential length (CL) and width were chosen to satisfy the simulations. The cylindrical metallic NWs were prepared in bulk crystal structure and the wire axes were oriented in the (0 0 1) direction with appropriate radius in order to maintain their small size effect and structural stability. The GNR was initially located beside the metallic NW with a separation distance of 8.0 Å (within the vdW cutoff distance). The axes of GNR and NW were parallel. Thereafter, MD simulations were performed to investigate the self-assembly of GNRs guided by NWs. During the calculations, data were collected every 0.1 ps to record the full-precision trajectory for further analysis.

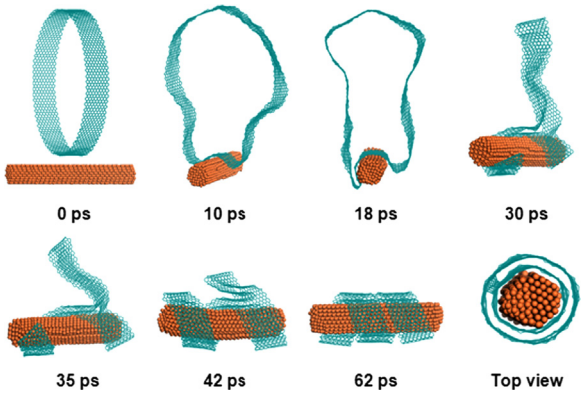

Fig. 1. Representative snapshots of a GNR self-assembling onto the Ni NW to form helical configuration and the top view of the snapshot at $t=62$ ps.

3. Results and discussion

The present work aims to reveal the self-assembly of bilayered helical nanostructures and especially the corresponding properties at an atomic level by exploring the GNR spontaneously scrolling onto metallic NWs in detail. Take Ni NW for example and the diameter is 13 Å. The CL of the armchair GNR is 340.38 Å and the width is 19.68 Å. As shown in Fig. 1, the overall simulation snapshots reveal quite a fast self-assembly process of GNR onto the Ni NW. As soon as the calculation starts, GNR displays discontinuous ripples and wrinkles several nanometers thick because of edge stress. Synchronously, the GNR and the Ni NW approach each other due to the strong attraction force. The surface closer to the Ni NW endures stronger vdW attraction and moves rather faster than the other part of the surface. Therefore, the circular cross-section of GNR deforms as an oval along the approaching direction. After the closer side of the GNR tightly adheres onto the NW, the top CNT surface will keep approaching the Ni NW due to the continuity of the ring resulting in the collapsing of GNR to a saddle in the cross-section, as shown in 10 ps snapshot in Fig. 1. When $t=18$ ps, the GNR starts to deflect and the left side of GNR walls attach to each other due to the offset π–π stacking effect. Thereafter, the collapse is further accelerated. When the simulation time is up to $t=30$ ps, the opposing walls of the rest of the GNR part also attach to each other. It is worth noting that the GNR has displayed a clear helical shape on the Ni NW surface with large pitch, trying to occupy the entire NW. As time goes on, two attached GNR walls are gradually separated from the each other to wrap around the NW owing to the stronger attraction from the NW and the spiral becomes denser (30–42 ps). It suggests that the vdW attraction between the GNR and the NW should be stronger than the π–π stacking interaction between GNR walls. Eventually, at $t=62$ ps, the GNR forms a bilayered helix (see the top view), with remarkably constant pitch and gap of 3.5 Å between the neighboring spirals, and wraps around the Ni NW surface. It is worth noting that the fringes at the two helixal ends become dimmer toward the inside to form two highly strained bulbs. The self-assembled GNR–NW system achieves its dynamic equilibrium through the spontaneous wrapping. This helix-forming process is irreversible no matter whether the final GNR–NW composite nanostructure is cooled or heated to any point of temperature. The handedness of the GNR helix is