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Hydrogenation enabled scrolling of graphene

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Abstract

Hydrogenation of graphene leads to local bond distortion of each hydrogenated carbon atom. Therefore, programmable hydrogenation of graphene can open up new pathways to controlling the morphology of graphene and therefore enable the exploration of graphene-based unconventional nanomaterials. Using molecular dynamics simulations, we show that single-sided hydrogenation can cause the scrolling of graphene. If a proper size of the graphene is hydrogenated on one side, the graphene can completely scroll up into a carbon nanoscroll (CNS) that remains stable at room temperature. We perform extensive simulations to delineate a diagram in which three types of scrolling behaviour of partially single-sided hydrogenated graphene are identified in the parameter space spanned by the hydrogenation size and the graphene size. Such a diagram can serve as quantitative guidelines that shed important light on a feasible solution to address the challenge of fabricating high-quality CNSs, whose open topology holds promise to enable novel nanodevices.

(Some figures may appear in colour only in the online journal)

S Online supplementary data available from stacks.iop.org/JPhysD/46/075301/mmedia

1. Introduction

Graphene's two-dimensional structure exposes its entire volume to its surrounding, rendering highly amenable surface Tremendous efforts have been placed on the chemistry. chemical functionalization of pristine graphene by adsorbing foreign atoms, molecules and functional groups on its surface [1-7], motivated by the great potential of controllably tailoring the electronic structure of graphene. In particular, hydrogenation of graphene involves attaching atomic hydrogen to the carbon atoms in graphene. As a result, the hybridization of carbon atoms in graphene is changed from sp² into sp³ and the two-dimensional atomic structure of pristine graphene is distorted into three-dimensional locally at each adsorbed hydrogen atom [1]. Significant progress has been made on controlled hydrogenation of graphene, with the aim to fine-tune graphene properties. For example, single-sided hydrogenation of pristine graphene has been demonstrated [1, 8-11]. Hybrid superlattices made of patterned hydrogenation of a pristine graphene can be fabricated in a controlled fashion on both macroscopic and microscopic scales [12]. This progress on programmable hydrogenation of graphene opens up new pathways to controlling the morphology of graphene and therefore enabling the exploration of graphene-based novel nanomaterials. In this paper, we demonstrate spontaneous scrolling of graphene enabled by single-sided hydrogenation, using molecular dynamics simulations. We show that, by controlling the size and shape of the hydrogenated region, a graphene nanoribbon can spontaneously scroll up into a carbon nanoscroll (CNS). Results from this paper shed light on a simple and robust solution to address the challenge of fabricating high-quality CNSs, and therefore facilitating the realization of unconventional device concepts enabled by the open topology of CNSs.

A CNS is formed by rolling up a monolayer graphene into a spiral multilayer nanostructure, whose core size is highly tunable by relative sliding between adjacent layers [13, 14]. In other words, a CNS is topologically open, fundamentally distinct from a tubular CNT, which is topologically closed. The open and highly tunable structure of CNSs, combining with the exceptional mechanical and electronic properties inherited from the basal graphene [15, 16], has inspired an array of novel



Figure 1. (*a*) Side view (top) and top view (bottom) of the equilibrium shape of a graphene nanoribbon (green) with one row of hydrogenation (red) on the same side along an armchair line. The graphene folds along the hydrogenation line to about 160° . (*b*) Two rows of hydrogenation along neighbouring armchair lines on the same side result in further folding of the graphene nanoribbon to about 135° . (*c*) One row of hydrogenation along a zigzag line on the same side result in folding of the graphene nanoribbon to about 130° . (*d*) Two rows of hydrogenation along neighbouring zigzag lines on the same side result in further folding of the graphene nanoribbon to about 130° . (*d*) Two rows of hydrogenation along neighbouring zigzag lines on the same side result in further folding of the graphene nanoribbon to about 100° .

nano-device applications, such as hydrogen storage medium [17, 18], water and ion channels [19], ultrafast nano-oscillators [20, 21] and translational nano-actuators [22]. Enthusiasm aside, the realization of these promising applications hinges upon feasible and reliable fabrication of high-quality CNSs, which remains a significant challenge. A completely rolled-up CNS is energetically more favourable than its basal graphene in a planar form, given that the reduction in the van der Waals (vdW) interaction energy among carbon layers in the CNS overbalances the increase in strain energy due to the bending of graphene [13]. Formation of a CNS, however, requires a sufficiently large driving force to overcome the energy barrier for initial curling and rolling of the basal graphene before its continuous scrolling into a CNS. Existing chemical approaches to overcoming such an initial energy barrier to form CNSs include applying high-energy sonication to exfoliated graphite sheets [23] or immersing a SiO₂-supported graphene monolayer in isopropyl alcohol solution [24]. In general, these chemical approaches to fabricating CNSs suffer from possible contamination of chemical residue, and also the difficulty in controlling the rolling initiation and rolling direction. Concepts of physical approaches to fabricating CNSs involve using a CNT of suitable diameter [25] or a water nanodroplet [26] to overcome the initial energy barrier of graphene scrolling. These physical approaches, however, require precise positioning of the CNT or water nanodroplet at the edge of the basal graphene, which is rather challenging.

Hydrogenation of a carbon atom in pristine graphene produces an sp^3 carbon-hydrogen (C-H) bond, which gives

rise to a local structural change around that carbon atom. Specifically, the chemically adsorbed hydrogen atom attracts its bonded carbon atom while it repels other neighbouring carbon atoms. As a result, the three initially planar carboncarbon (C-C) bonds associated with the hydrogenated carbon atom are distorted and locally bend away from the hydrogen atom. If hydrogen atoms are chemically adsorbed by the carbon atoms in pristine graphene on both its sides in an alternative manner, the resulting hydrogenated graphene (termed as graphane [1, 27, 28]) overall remains a rather planar morphology as the local out-of-plane distortion of the C-C bonds cancel each other. However, if the graphene is singlesided hydrogenated, the local distortion at each hydrogenated carbon atom is accumulated [29]. As a demonstration of such an accumulated effect, figure 1 shows that a graphene nanoribbon with one row of hydrogenation on the same side along an armchair line folds up to about 160°, while two rows of hydrogenation along neighbouring armchair lines on the same side result in further folding of the graphene nanoribbon to about 135°. Similarly, one row of hydrogenation along a zigzag line on the same side results in folding of the graphene nanoribbon to about 130°, while two rows of hydrogenation along neighbouring zigzag lines on the same side result in further folding of the graphene nanoribbon to about 100°. Results in figure 1 suggest that if sufficient carbon atoms in the graphene are hydrogenated on one side, the graphene morphology can be altered in a manner curving towards another side. Furthermore, if the curving of the graphene can be achieved in a controlled fashion, it can serve as a feasible approach to overcoming the initial energy barrier of graphene scrolling into a CNS. To explore such a promising approach to addressing the challenge to fabricate high-quality CNSs, we perform systematic molecular dynamics simulations to investigate the hydrogenation enabled scrolling of graphene, with particular focus on deciphering the key parameters that govern the successful scrolling of graphene into CNSs.

2. Results and discussion

Figure 2(a) depicts the simulation model of a graphene of length L and width W that is single-sided hydrogenated at one end for a length of L_h . In each carbon hexagon in the hydrogenated region, one hydrogen atom is chemically bonded to each of the three carbon atoms in alternating lattice positions (see the inset of figure 2). Therefore, half of the carbon atoms in the hydrogenated region are bonded with hydrogen atoms on the same side. In the simulations, the C-C and C-H bonds in the graphene as well as the non-bonded C-C and C-H interactions are described by the Adaptive intermolecular Reactive Empirical Bond Order (AIREBO) potential [30]. Molecular dynamics simulations of the graphene scrolling are carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [31] with canonical ensemble at a temperature of 300 K. Before running dynamic simulations, the energy of the system is first minimized using the conjugate gradient (CG) algorithm until either the total energy change between successive iterations divided by the energy magnitude is less than or equal to 10^{-6} or



Figure 2. (a) Simulation model of a graphene of a length L and a width W that is single-sided hydrogenated at one end in a length of L_h . The inset shows the detailed lattice structure of the hydrogenated region. (b) Energy minimized structure of the model.

the total force is less than 10^{-5} eV Å⁻¹. The energy minimized structure is shown in figure 2(*b*).

We first consider a square shaped graphene, i.e. L = W, and investigate the effect of the length of the hydrogenated region $L_{\rm h}$ on the scrolling of such a graphene. Emerging from the simulation results are three types of scrolling behaviour of partially single-sided hydrogenated graphene, as shown in figure 3. Here, L = W = 12 nm. If the length of the hydrogenated region $L_{\rm h}$ is just a small fraction of the graphene width, (e.g. $L_h/W = 0.3$), the graphene can only scroll up partially. Figures 3(a)-(d) plot the sequential snapshots of the graphene at 1 ps, 5 ps, 28 ps, and 47 ps in the simulation, respectively. At the beginning, all three free edges of the rectangular hydrogenated region curl up towards the opposite side of hydrogenation (figure 3(a)). The curling of the long free edge then becomes dominant and leads to the scrolling of the hydrogenated portion of the graphene (figures 3(b)-(d)), driven by both the hydrogenation-induced local lattice distortion and the reduction in the vdW interaction energy among the atoms in the hydrogenated region, as clearly indicated by the decrease in potential energy of the system in figure 3(e) (from state (a) to state (d)). Note that at the end of the partial scrolling process of the hydrogenated portion (figure 3(b)), the translational kinetic energy of the partial scroll leads to the tendency of further scrolling of the graphene over the pristine region. However, this further scrolling is at the price of further increase in the graphene strain energy, which roughly scales with the square of the graphene curvature. For a small value of L_h (e.g. 3.6 nm in figures 3(a)-(d)), the radius of the partially scrolled graphene in the hydrogenated region (e.g. figure 3(b)) is small, indicating a large curvature of graphene if further scrolling occurs, which leads to an increase in the strain energy of the graphene that outweighs the reduction in the vdW interaction energy among the carbon layers. Without sufficient driving force, the partial scroll oscillates back and forth for a few times (as indicated by the fluctuation of the potential energy profile in figure 3(e)) before the excess translational kinetic energy is dissipated. At the steady state, scrolling only occurs in the hydrogenated region of the graphene and the pristine region remains planar (e.g. figure 3(d)).

If single-sided hydrogenation is introduced in a proper size in the graphene (e.g. $L_{\rm h}/W = 0.4$), the initial scrolling of the hydrogenated region results in a partial CNS of relatively larger radius, leading to a modest increase in the graphene strain energy in further scrolling process that can be sufficiently driven by a further reduction in the vdW interaction energy among carbon layers. As a result, continuous scrolling proceeds throughout the whole graphene, leading to the formation of a CNS that remains stable at 300 K, as illustrated in figures 3(f)-(j). However, if the hydrogenated region is too large (e.g. $L_{\rm h}/W = 0.8$), the three free edges of such a region are of comparable length, and therefore the curling up and subsequent scrolling of these three edges indeed constrain each other (e.g. figures 3(k)-(m)), preventing the dominant scrolling of one edge and thus the formation of a complete CNS. Eventually the graphene rolls up into an irregular nanostructure (figure 3(n)).

We next carry out systematic molecular dynamics simulations to explore the scrolling behaviours of a squareshaped graphene of a wide range of size (from 6 to 21 nm) with various sizes of hydrogenated area (i.e. L_h/W ranges from 0.2 to 0.8). Figure 4 shows the morphology of these graphene at equilibrium. Emerging from the parametric study are the same three types of scrolling behaviour of partially single-sided hydrogenated graphene as depicted in figure 3. Furthermore, it turns out that for a given size of square-shaped graphene, its scrolling behaviour depends strongly on the relative size of the hydrogenated region (i.e. L_h/W) rather than its absolute size (i.e. L_h).

Figure 5 plots a diagram of the three types of scrolling behaviour of partially single-sided hydrogenated graphene in



Figure 3. Three types of scrolling behaviour of partially single-sided hydrogenated graphene. Here L = W = 12 nm. When $L_h/W = 0.3$, the graphene can only scroll up partially, as shown in sequential snapshots of the graphene morphology at (a) 1 ps, (b) 5 ps, (c) 28 ps and (d) 47 ps, respectively. When $L_h/W = 0.4$, the graphene can completely scroll up into a CNS, as shown in sequential snapshots of the graphene morphology at (f) 1 ps, (g) 9 ps, (h) 13 ps and (i) 50 ps, respectively. When $L_h/W = 0.8$, the graphene scrolls into an irregular nanostructure, as shown in sequential snapshots of the graphene morphology at (k) 1 ps, (l) 3 ps, (m) 13 ps and (n) 52 ps, respectively. (e), (j) and (o) plots the evolution of the system potential energy as simulation time for the above three cases, respectively. See the online supporting information (stacks.iop.org/JPhysD/46/075301/mmedia) for the molecular dynamics simulation videos of the above three cases.

the parametric space spanned by L_h/W and W. If the graphene size is sufficiently large (e.g., $W \ge 12$ nm), there exists a range of the relative size of the hydrogenated region (i.e. $0.4 \le L_h/W \le 0.6$), in which the partially hydrogenated graphene can successfully scroll up into a complete and stable CNS (similar as in figure 3(i)). Such a range of value of L_h/W is approximately independent of the graphene size. If the hydrogenated region is too small (i.e. $L_h/W < 0.4$), only the hydrogenated region can scroll up while the pristine region of the graphene remains planar (similar as in figure 3(d)). If the hydrogenated region is too large (i.e. $L_h/W > 0.6$), the competing curling up and scrolling of the three free edges eventually result in an irregular nanostructure (similar as in figure 3(n)).

By contrast, if the graphene size is small (e.g. W < 12 nm), the partially single-sided hydrogenated graphene can

either only partially scroll up the hydrogenated region if $L_{\rm h}/W < 0.6$ or scroll into an irregular nanostructure if $L_{\rm h}/W > 0.6$. In other words, the graphene of a small size cannot completely scroll up into a stable CNS. This can be understood as follows. As the graphene size decreases, in addition to the aforementioned energetic competition between the increasing strain energy and the decreasing vdW interaction energy of the graphene, the intrinsic edge ripples in the graphene becomes more significant in the energetic interplay to determine the graphene scrolling behaviour. The nature of the bonding structure of the free edges in graphene dictates an intrinsic compressive edge stress along the edges, resulting in the ripples along the free edges of the graphene [32]. In other words, rolling up graphene involves smoothing down (at lease partially) the intrinsic edge ripples, posing additional energy barrier to the scrolling process. While the driving



Figure 4. The equilibrium morphology of a square-shaped graphene of a wide range of size (from 6 to 21 nm) with various sizes of hydrogenated area (i.e. L_h/W ranges from 0.2 to 0.8).



Figure 5. A diagram of the three types of scrolling behaviour of partially single-sided hydrogenated graphene in the parametric space spanned by $L_{\rm h}/W$ and W.

force of further scrolling of graphene roughly scales with the graphene width, the additional energy barrier due to the intrinsic ripples along the two edges along the scrolling direction is approximately independent of the graphene size. Therefore, there exists a critical graphene size, below which there is no sufficient driving force to overcome the energy barriers due to edge ripples. As a result, the graphene cannot completely scroll up into a stable CNS. To understand the finding that the scrolling behaviours

of partially single-sided hydrogenated graphene depends on

 $L_{\rm h}/W$ rather than $L_{\rm h}/L$, figures 6(a)-(d) and (e)-(h) compare

the scrolling behaviours of two graphene nanoribbons with

the same values of L = 21 nm and $L_h = 8.4 \text{ nm}$ (thus

 $L_{\rm h}/L = 0.4$) but different values of W (12 nm and 21 nm,

thus $L_{\rm h}/W = 0.7$ and 0.4, respectively). In both cases, all

three free edges of the hydrogenated portion tend to curl up at

the initial stage. For the case of a large ratio $L_h/W = 0.7$ (figures 6(a)-(d)), the sizes of such three free edges are

comparable, so are the driving forces for further scrolling of the

three edges. Consequently, the competing further scrolling of these three edges results in an irregular nanostructure. For

the case of a small ratio $L_{\rm h}/W = 0.4$ (figures 6(e)-(h)),

however, the free edge of the hydrogenated portion at the

left end of the graphene nanoribbon is much longer than the other free hydrogenated edges. As a result, the further

scrolling of this long free edge gains more momentum that is



Figure 6. (*a*)–(*d*) Morphologic evolution of a partially single-sided hydrogenated graphene nanoribbon (L = 21 nm, $L_h = 8.4 \text{ nm}$ and W = 12 nm), which ends up as an irregular nanostructure. (*e*)–(*h*) Morphologic evolution of a graphene nanoribbon (L = 21 nm, $L_h = 8.4 \text{ nm}$ and W = 21 nm), which fully rolls up into a stable CNS. (*i*)–(*l*) Morphologic evolution of a graphene nanoribbon (L = 21 nm, $L_h = 6.3 \text{ nm}$ and W = 21 nm), which can only partially roll up the hydrogenated portion (highlighted in red). Perspective views from the side in (*k*) and (*l*) reveal that the partial CNS tends to bend towards its outer edge that separates the hydrogenated and pristine portions of the graphene.

Figure 5 shows that there exists a minimum length of the hydrogenated portion of the graphene nanoribbon, below which the partial scrolling of the hydrogenated portion cannot proceed further to roll up the pristine portion. To shed light on the theoretical understanding of this finding, we consider a simple analytic model to estimate the minimum radius of the partial scroll that can proceed further. As discussed above, the further scrolling is governed by the competition between the increase in elastic energy of the pristine portion of graphene and the decrease in the interfacial energy of the system. An infinitesimal increment of the radius of the scrolled part dR leads to a bending-induced increment of elastic energy $dE = (\pi DW/hR) dR$, where D is the bending rigidity of pristine graphene and h is the equilibrium interlayer distance of graphene, and an increment of interfacial energy $d\Gamma$ = $2\pi\gamma W dR$, where γ is the surface energy of graphene. The equilibrium of total energy determines a critical radius $R_{cr} =$ $D/2\gamma h$, above which further scrolling becomes energetically favourable. Taking $D = 0.225 \,\mathrm{nN}\,\mathrm{nm}, \,\gamma = 0.4\,\mathrm{N}\,\mathrm{m}^{-1}$ and h = 0.34 nm, one obtains $R_{\rm cr} \approx 0.83$ nm. Such an estimate agrees well with the prediction from figure 5. For example, for the case of L = W = 12 nm and $L_{\rm h} = 4.8$ nm, molecular dynamics simulation shows that the radius of the partial scroll of the hydrogenated portion is about 0.8 nm and it can further

and $L_{\rm h} = 3.6\,\rm nm$, simulation shows that the radius of the partial scroll is about 0.5 nm and the pristine portion of the graphene nanoribbon remains unscrolled at steady state. Note that as the width of the graphene nanoribbon increases, the above simple analytic consideration tends to underestimate the minimum length of the hydrogenated portion to allow further scrolling. For example, as shown in figures 6(i)-(l)(L = W =21 nm and $L_{\rm h} = 6.3$ nm), even though the radius of the partial scroll is greater than the predicted critical value of 0.8 nm, it still cannot further roll up the rest of the graphene nanoribbon. Figures 6(k)–(l) reveal that a small value of $L_{\rm h}/W$ (= 0.3) dictates a slim partial scroll that tends to bend towards its outer edge that separates the hydrogenated and pristine portions of the graphene as an effort to further release the hydrogenationinduced lattice distortion. The curved profile of the partial scroll imposes further energy barrier and thus prevents further scrolling. On the other hand, a larger value of $L_{\rm h}/W$ (= 0.4) leads to a thicker partial scroll that is stiff enough to remain roughly straight and thus can continue rolling up the rest of the graphene nanoribbon, as predicted by simulation results in figures 4 and 5. The above discussion further explains that

proceed to roll up the whole graphene nanoribbon into a

complete CNS. By contrast, for the case of L = W = 12 nm



Figure 7. The evolution of the system potential energy of $12 \text{ nm} \times 30 \text{ nm}$ partially single-sided hydrogenated graphene as a function of simulation time. The hydrogenation enabled scrolling causes continuous decrease in the potential energy, leading to a complete CNS that remains stable at 300 K. See the online supporting information (stacks.iop.org/JPhysD/46/075301/mmedia) for the molecular dynamics simulation video of the scrolling process.

the scrolling behaviour of partially single-sided hydrogenated graphene depends strongly on L_h/W , rather than L_h .

We then further investigate the effect of the length of the partially single-sided hydrogenated graphene on its scrolling behaviour. To this end, we increase the length of the graphene for those simulation cases in figure 5, so that L > W. We find that the simulation results are rather similar to those described in figure 5. For example, if square shaped graphene with a proper size of the hydrogenated region (i.e. $0.4 \leq L_h/W \leq$ 0.6) can completely scroll up into a stable CNS, so does rectangular graphene with the same values of W and $L_{\rm h}/W$ but a larger value of L > W. As a demonstration, figure 7 plots the scrolling process of partially single-sided hydrogenated graphene (W = 12 nm, L = 30 nm and $L_h/W = 0.4$) along with the evolution of the total potential energy of the system. After the hydrogenated region scrolls up, the rolling process continues until the complete formation of a CNS that remains stable at 300 K. The negligible effect of the length of graphene on its scrolling behaviour can be readily explained as follows. Once the scrolling can proceed into the pristine region of the graphene, further scrolling involves wrapping of the graphene around a partial CNS of increasing radius. In other words, the energy barrier for further scrolling is ever decreasing. By contrast, the driving force for further scrolling remains roughly unchanged. Consequently, rectangular graphene with a proper size of the hydrogenated region can always completely scroll up into a stable CNS. In this sense, the diagram in figure 5 can also be applicable to predict the scrolling behaviours of rectangular graphene.

3. Summary

We demonstrate the spontaneous scrolling of graphene that is partially hydrogenated on one side, using molecular dynamics simulations. The curling up and scrolling of the hydrogenated

region of the graphene is due to the accumulated effect of the local lattice distortion in the graphene at each adsorbed hydrogen atom. We show that, if a proper size of the graphene is single-sided hydrogenated, the scrolling of the hydrogenated region can proceed continuously into the pristine region of the graphene and further throughout the whole graphene. As a result, the graphene scrolls into a complete CNS, which remains stable at room temperature. Systematic parametric study leads to a diagram in the space of the relative size of the hydrogenated region and the graphene width that delineates three types of scrolling behaviour of partially single-sided hydrogenated graphene. Such a diagram can serve as quantitative guidelines that shed important light on a feasible and promising solution to address the challenge of fabricating high-quality CNSs. Since hydrogenation is a reversible process, the chemically adsorbed hydrogen can be evaporated at an elevated temperature. The resulting CNS from the scrolling of partially hydrogenated graphene could be potentially further treated to be hydrogen free while maintaining its scrolled form, as a CNS has a lower energy than its basal pristine graphene. With the ever maturing nanopatterning technique to hydrogenate graphene at high spatial resolution and precision [12, 33], the hydrogenationenabled formation of CNSs holds great potential to enable further applications of CNS-based novel devices.

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