Atomistic insights into the nanohelix of hydrogenated graphene: formation, characterization and application

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Hydrogenated graphene has been emerging as the cynosure of the subject for numerous studies due to its conductivity, ferromagnetism, and potential for energy storage as well as drug delivery. However, how to find a decent way to overcome the graphene bending barrier and modify graphene from planar structures to 3D structures remains to be further explored. By virtue of molecular mechanics/dynamics simulations, here we present the formation of a carbon nanohelix from a pristine graphene nanoribbon by doping it with hydrogen atoms in a specific pattern. Meanwhile, we quantitatively investigate the effect of the interatomic potential on the process of helical structure formation, thermal stability and mechanical properties of the carbon nanohelix as well as its potential application in molecule packing. The carbon nanohelix portrays an intriguing zigzag strain–stress curve and amazing extensibility under tension as well as relatively limited deformability under compression, which represents its unique signature of mechanical properties to differentiate the carbon nanohelix from the behavior of the carbon nanotube and graphene. These findings lend compelling credence to envision that the carbon nanohelix opens up a viable avenue for nanofabrication and is perceived as a novel nanomaterial for a variety of applications such as electronics, sensors, energy storage, drug delivery and nanocomposites.

1. Introduction

The nature of unprecedented functional properties of graphene, such as electronic, magnetic, mechanical, and thermal properties, is determined to a large extent by its unique two dimensional graphene morphology. In recent years, tremendous efforts have been devoted to manipulate the graphene morphology, such as graphene folding by growth and transfer from patterned surfaces, ion radiation, capillary forces, mechanical strain and chemical functionalization, to controllably design various 3D architectures of graphene.

The chemical functionalization of a pristine graphene sheet by absorbing hydrogen atoms attracts extensive attention since hydrogenation creates local geometric distortion on the graphene by changing hybridization from sp² to sp³. Significant simulation work has been done for precisely controlled hydrogenation in view of hydrogenation style. Double side-hydrogenation with alternating actions transfers the pristine inert semi-metal graphene into the insulator, while one side of hydrogenation of graphene becomes a ferromagnetic semiconductor by breaking down the delocalized π-bonding network of graphene. By changing the size of the hydrogenation area, patterned graphene domain arrays embedded in a graphene sheet could serve as the template to precisely position and pack the molecules. A proper size of single-side hydrogenation can completely scroll up into a stable carbon nanoscroll under room temperature. However, generating a helical structure by chemical functionalization remains unexplored.

Helix is an omnipresent but mysterious structure among a myriad of fields in nature. For instance, helical structures have gained appreciable popularity in biology systems for a wide variety of applications, ranging from ubiquitous helical strand structures for supporting right-handed polynucleotide chains in DNA to higher order assemblies such as α-helix secondary proteins for providing a vast array of functions in living organisms. The double helix has been perceived as an indispensable building block for the construction of complex biological elements. Two strands are mutually backed up to each other therefore the damage on one strand can be repaired by attaching another fundamental base. In the electric field, the twisted-pair cable is the most important transmission medium due to their low electromagnetic interference and energy loss. The spring, exerting a proportional force to the change of length, displays outstanding elastic properties and stores mechanical energy. A zinc oxide (ZnO) nanohelix that resembles the helical configuration of DNA forms a new type of band structure, thereby providing...
novel ways to create nanometre-scale sensors, transducers and resonators.\(^{14}\) The coiled Si nanowires have been demonstrated with a constant electrical response which accommodates large tension, compression, bending and twisting, and offers promising potential for fabricating stretchable electronics.\(^{15}\) Graphene nanoribbons can display DNA-like configuration with encapsulation of the carbon nanotubes due to the vdW potential well and \(\pi-\pi\) stacking interactions.\(^{16}\) By quantum molecular dynamics simulations and classical continuum-elasticity modelling, the graphene nanoribbons have been transformed into carbon nanotubes by means of mechanical twisting.\(^{17}\) The twisted graphene nanoribbons have demonstrated enhanced stretchability due to non-linear deformation of the covalent C-C bond.\(^{18}\) Very limited endeavours have been devoted to investigate the properties of the helix and reconstruct the helix at the nanoscale. Also, finding an effective and spontaneous way of generating a helical structure with a single graphene sheet is still challenging. Here, in our study, an intriguing carbon nanohelix is formed by chemical functionalization in way of simulation. Novel functionalization patterns have the potential to lead to astounding new capabilities, and deserve intensive investigation in order to maximize the capabilities of graphene-based devices. Meanwhile, by performing molecular mechanics/dynamics simulation, we will present the mechanism of the spontaneous formation of helical carbon nanotubes by controlling the hydrogenated region and doped patterns on a graphene nanoribbon, characterize its thermal and mechanical properties, and extend its utilization for molecule packing as a promising application.

2. Method

In the simulation, the powerful and popular Amber force field in the LAMMPS package is used to describe the bonded and non-bonded interactions between the chemical elements. The Amber force field has been described to provide a quantitatively accurate description of C-C and C-H bond interaction as well as covalent bond formations/breaking during the simulation due to doped foreign atoms and/or mechanical loading. The potential components described in the Amber force field with specific parameters are defined as

\[
E_{\text{total}} = \sum \kappa_b (\ell - \ell_0)^2 + \sum \kappa_\alpha (\theta - \theta_0)^2 \\
+ \sum \frac{1}{2} \kappa_\gamma [1 + \cos(m\phi - \gamma)]^2 \\
+ \sum_{j=1}^{N} \sum_{i=j+1}^{N} \left\{ \epsilon_{ij} \left[ \left( \frac{r_{ij}}{r^*_{ij}} \right)^{12} - 2 \left( \frac{r_{ij}}{r^*_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}
\]

where the first three terms account for intramolecular interactions (bond stretch, bond angle, dihedral angle) characterizing the short-range bonding while the last two terms are associated with intermolecular interactions describing the long-range van der Waals (vdW) interactions and electrostatic interactions. Typically, 12-6 Lennard-Jones potential is adopted to describe the vdW interaction based on the Lorentz–Berthelot mixing rule. To terminate the unphysical high bond force arising from improper cutoff functions, we set the cutoff as 8 Å, and periodic boundary conditions are also applied in the simulation. The time step is set as 0.1 fs. To achieve the most favorable structures of graphene after doping foreign atoms, a conjugate gradient algorithm has been employed to perform energy minimization until the total energy change between two successive iterations divided by the energy magnitude is less than or equal to \(10^{-10}\).

Initially, a pristine rectangular (6, 6) graphene nanoribbon 24.9 Å \(\times\) 195.7 Å is constructed. Along the zigzag direction (x-axis), the hydrogen atoms are covalently decorated at a distance of 1.09 Å above the carbon atoms every other single and double armchair line in the z direction. Fig. 1 shows a graphene sheet with two single-sided doped patterns; Fig. 1(a) is doped hydrogen atoms with high density every other single armchair line while Fig. 1(c) shows doped hydrogen atoms with low density every other double armchair line. The yellow colour represents the hydrogen atoms while the rest represents the bonded carbon atoms. For the purpose of illustration, the carbon atoms on both edges of the graphene sheet are coloured as blue. Due to the enormous ratio of length to width of the graphene nanoribbon, it becomes difficult to bend the graphene nanoribbon along x or y direction except along the z direction. By applying the molecular mechanics simulation, the two ends of graphene firstly tend to bend perpendicularly out of the x-z plane. The stacking effect between two graphene sheets and vdW interaction between the hydrogen and carbon atoms both contribute to forming the preferable helical structure. The hydrogenated graphene nanoribbon eventually forms into a carbon nanohelix by starting from both ends of the graphene sheet as depicted in Fig. 1(b) and (d). It can be noticed that the radius and smoothness of the helical tube strongly depend on the hydrogen doping density and chirality of the graphene nanoribbon. Here we use graphene nanoribbons with the same length of 195.67 Å for each simulation. For the high doped density of hydrogen atoms, Fig. 1(b) shows a helical tube with radius 12.06 Å and smooth surface while Fig. 1(d) shows the structure with radius 14.58 Å and relatively rough surface by low doped density. Fig. 2 depicts the final helical tubes from the graphene nanoribbons with chirality (5, 5), (6, 6), (7, 7), (8, 8), and (9, 9), respectively. The corresponding radii of these carbon nanohelices are 11.15, 12.98, 13.98, 15.53, and 16.06 Å, respectively, which indicates that the radius of the carbon nanohelix formed by the graphene sheet increases with the index of chirality going up. To better present the geometry of the carbon nanohelix, a helix unit is defined as the unit between two gap intervals that is distinguished by the carbon atoms with blue colour in Fig. 2. The length of the helix unit of each nanohelix is 25.53, 28.97, 36.85, 49.88, and 63.35 Å, respectively, which suggests that the helix unit heavily relies on the chirality of the graphene sheet. These findings provide a feasible way to create a plethora of 3D nanohelix with different architectures from a single doped graphene sheet. To better understand the properties of the carbon nanohelix, the effects of interatomic potential on hydrogenated graphene, thermal stability and mechanical properties of a
carbon nanohelix will be discussed in the following sections. For the sake of simplicity and clarification, we will focus on hydrogenated graphene with chirality (6, 6) to present the discussion.

3. Results and discussion

3.1. Interatomic potential on initial hydrogenated graphene

In what follows, we first investigate the interatomic potential on initial hydrogenated graphene with chirality (6, 6) (80 Å × 25 Å) under a specified doping pattern. Hybridization from sp2 to sp3 after hydrogenation provides an appreciable driving force to tackle the energy barrier of graphene bending. After the sp2 to sp3 hybridization in which the other three bonds are constrained by the surrounding carbon atoms, hydrogenation leads to a nearly tetrahedral arrangement which pushes the graphene towards the opposite side of doped hydrogen. Besides, the single-sided hydrogenation pattern accumulates the distortion around the bonded carbon atoms from one side which accelerates the out-of-plane bending. To investigate the fundamental driving force to fulfill the graphene scrolling process, here we devote our efforts to exploring how the interatomic potential components in eqn (1) affect the graphene scrolling process. The energy distribution contour plot aims to determine that the angle bending energy is a dominating factor for the out-of-plane bending of hydrogenated graphene.

The angle bending energy involving hydrogenated carbon atoms increases spontaneously and the local structure seeks an energetically preferential state wherein all covalent bonds seek to be as far from each other as possible. At the beginning, the angle bending energy releases to overcome the energy barrier of graphene bending and tends to fold and scroll the graphene nanoribbon. Due to the large ratio of the graphene nanoribbons, folded graphene nanoribbon favourably forms the twisted stack and the rearrangement of hydrogenated carbon atom continues to bend the graphene nanoribbon into the helical structure. For example, the graphene nanoribbon with chirality (9, 9) shown in Fig. 2 fails to overcome the energy barrier and forms a stable helix as graphene nanoribbons with chirality (5, 5) and (6, 6) do. Therefore, the energy distribution is critical to demonstrate the formation of helical structures.

Fig. 3(a) shows the contour profile of total energy distribution of the carbon atoms on pristine graphene while Fig. 3(b) shows the contour profile of the total energy of carbon atoms after hydrogenation. In the pristine graphene, as shown in Fig. 3(a), the total energy of the carbon atom is identically 21.38 kcal mol⁻¹ except for the carbon atoms on the edge of graphene which have weaker interactions with the other carbon atoms than the interior carbon atoms. Fig. 3(b) highlights that the carbon atoms in the doped area switch the average energy from 21.38 to 56.97 kcal mol⁻¹ as shown in red color in Fig. 3(b).
The carbon atoms outside the hydrogenation area are slimly affected due to the cutoff distance. Fig. 3(c) depicts the contour profile of the angle bending energy on each carbon atom while Fig. 3(d) depicts the sum of the rest energy components described in eqn (1). The average of the angle bending energy on the carbon atoms in hydrogenation regions changes profoundly from 2.13 kcal mol\(^{-1}\) before hydrogenation to 45.76 kcal mol\(^{-1}\) after hydrogenation. Intriguingly, all the rest energy components remain almost unaffected from 19.26 kcal mol\(^{-1}\) before hydrogenation to 17.96 kcal mol\(^{-1}\) after hydrogenation. Fig. 3 demonstrates that the
accumulated angle bending energy by hydrogenation makes a prominent contribution to generate the helical structure.

Fig. 4 shows the change of the total energy of a system of two types of doped patterns during the formation of a helical graphene structure. Initially, the system possesses enormous bending energy after the hydrogenation. Due to transition from sp$^2$ to sp$^3$ bonding of the hydrogenated carbon atoms, hybridization deforms the local hexagonal carbon structures by creating geometric distortion. The hydrogenated graphene reshapes instantly when the simulations start. The total energy of the system drops quickly at first, and then decreases smoothly when the two ends of the graphene nanoribbon scroll up simultaneously until the final helical structure is generated.

### 3.2. Thermal stability

Materials and structures that possess outstanding thermal properties have emerged as an essential building block of a new generation of devices, especially at the nanoscale. Therefore, it is worthwhile to investigate the thermal stability of the novel structure, carbon nanohelix, for potential electrical and thermal implications. Here we perform MD simulation to study the thermal stability of a nanohelix system under a variety of temperatures. The nanohelix is heated continuously from 0 to 1000 K with a unit step increase of 100 K for a certain period of 100 ps. That means the nanohelix will equilibrate for 100 ps at each new temperature. From the simulation results, the carbon nanohelix maintains its stable structure until 900 K, and its bonds begin to break at temperature 1000 K, which is comparatively in agreement with the experimental results, documenting that the dehydrogenation temperature of graphene is observed near 700 K by Elias et al.\(^9\) Also the helix remains stable as the hydrogen atoms are removed from the carbon nanohelix. This study suggests the carbon nanohelix is stable at room temperature, thereby offering important insights into the multi-complex electrical and mechanical applications related to the thermal issues of carbon structures.

### 3.3. Strain–stress relationships under tension and compression

Numerous compelling experimental evidence demonstrates that the carbon nanotube and graphene possess extraordinary mechanical properties. For instance, the averaging Young’s modulus of an individual carbon nanotube ranges from 0.4 to 4.15 TPa with different experimental parameters and measurement techniques.\(^19,20\) The Young modulus of pristine graphene is 1.0 ± 0.1 TPa.\(^21\) The elasticity of hydrogenated graphene is quite different from the pristine graphene since hydrogenation causes local geometrical changes and therefore the behavior of the loading capacity changes.\(^22\) The morphological change from a graphene nanoribbon to a carbon nanohelix plays a crucial role in the mechanical properties. The spring-like structure of the carbon nanohelix demonstrates extraordinary capability for large deformations along the loading direction during the tensile process. Intuitively, it is interesting to study the mechanical properties of this type of helical structure which has an identical shape to springs we encounter in daily life. The helical structure with length 219.05 Å from (6, 6) hydrogenated graphene nanoribbon with length 338.43 Å, as shown in Fig. 5, is presented to investigate the mechanical properties of a nanohelix structure. The nanohelix has five typical helical units. During the simulation, one end of the nanohelix with length 48.36 Å, which is long enough to ensure the nanohelix doesn’t rotate when it is stretched and compressed, is chosen to be fixed. The other end of the nanohelix with length 46.68 Å is tethered with displacement 0.2 Å each time step along the z-axis direction. The remaining part of the helical nanotube is controlled as NVT ensemble with temperature 300 K. The C–C bond is set to be breakable when its length reaches 1.8 Å during the simulation.

Fig. 6 highlights the tantalizing zigzag strain–stress (SS) curve of the nanohelix under tension, which can serve as a
unique signature of the nanohelix to distinguish itself from the typical mechanical behavior of a carbon nanotube\textsuperscript{20} and a graphene nanoribbon.\textsuperscript{21} The representative signature of the nanohelix also sparks speculation of the fundamental mechanism behind this intriguing behavior.

In what follows, we strive to unravel the underpinning mechanism of the nanohelix which centers on the critical points of SS curve and the corresponding atomistic description of a local deformation change. From the beginning to point A on the SS curve in Fig. 6, it can be noticed that the nanohelix almost deforms uniformly with a stable atomistic configuration depicted in the snapshot A until the strain reaches 30%. The SS curve takes a smooth increase pattern with an estimated Young’s modulus of 105 GPa, which is quite lower than that of a carbon nanotube 1.0 TPa while the strain of the nanohelix at this point being close to that of the carbon nanotube at its fracture point.\textsuperscript{20} When the deformation of the nanohelix goes beyond 30%, a significant drop of the stress is observed on the SS curve which makes the first contribution to the landscape of an amazing zigzag SS curve. Snapshot B showcases the atomistic configuration of the nanohelix with a sudden giant gap between the two helix units, which is very similar to the snap-through instability of the shell structure.\textsuperscript{22} One of the reasons for this stress jumps behavior is the heterogeneous structure of the carbon nanohelix as compared with the pristine graphene structure. As the carbon nanohelix is formed from the hydrogenated graphene nanoribbon, the perfectly oriented hexagonal unit in the pristine graphene is broken and twisted into a non-symmetrical nanohelix. Due to the sparse hydrogenation in every other armchair or zigzag line, the twisted hexagonal units together with the intact hexagonal units form the rough surface of the helix which leads to a local protrusion and dent at the helical units. This characteristic feature in the nanohelix obviously distinguishes itself from the homogeneous graphene nanoribbon and carbon nanotube. Another reason is the weak and unstable interactions between the atoms on both sides of each helix unit. After the formation of the helix structure from the graphene nanoribbon, the carbon atoms at one edge of the graphene nanoribbon shown with blue color in Fig. 1 weakly interact with the adjacent carbon atoms from the opposite edge of the graphene nanoribbon. The carbon atoms forming the edge of the helical unit represent the unconstrained and non-uniform pair forces at the joints between the helical units which make pivotal contributions to the stress jumps in the nanohelix. When the carbon nanohelix is stretched, the edge carbon atoms between the helical units can not sustain the stress field, therefore triggering the instability of the helical units, in which the local crack-like dislocation between the local helical units increases accompanying the decreased interactions with edge carbon atoms on the other side of the helical units. The “snap-through” instability of the two adjacent edges of the nanohelix triggered by interaction of the hydrogen atoms sheds light on the dramatic drop of magnitude of the stress at point B. It can be noticed that Young’s modulus of the nanohelix retains the same value of 100 GPa after the drop due to the “snap-through” instability. Points A and B show clearly the evolution how the edge carbon atoms in one side of the helical units detach from the edge carbon atoms of the other side of the helical units and even separate further as the tensile process goes on. Therefore, the majority of carbon atoms in the interior of the carbon nanohelix with grey color are observed after the crack-like dislocation between the helical units becomes larger. Similarly, several cycles of stress drop happening at points C, D, and E are attributed to instability from the opening of two adjacent helical units. However, these local drops of the stress don’t affect the overall behavior of the SS curve. From the SS curve, it can also be observed that after point E the nanohelix becomes stronger with the increase of Young’s modulus from 100 to 150 GPa. A snapshot of the atomistic configuration at point G elicits interesting instability from the collapse of the helical units under extreme deformation with strain 133%, which represent the corresponding drop of stress in the nanohelix. Several similar stress decreases happen at points F and H before it reaches the yield point I with yield strength 156 GPa, portraying the whole intriguing picture of the zigzag SS curve of the nanohelix. It should be emphasized that Young’s modulus shows an unconventional increase after each stress drop at points F, G, and H. After the yield point, the nanohelix breaks into two pieces with a clean cleavage at the breakpoint depicted in snapshot J. It should be noticed that for homogeneous materials, the breakpoint normally happens in the middle section of the specimen under tensile loading. For example, usually the carbon nanotube is fractured at the middle position under the tensile process.\textsuperscript{24} However, the nanohelix presented here is a typical heterogeneous structure. Heterogeneous architecture in the nanohelix leads to local instability and therefore to an arbitrary fracture position along the axis of the nanohelix under the tensile process. The tensile test also informs that the nanohelix shows extreme deformability with strain 206% unmatched by other carbon-based nanomaterials or structures.

Meanwhile, Fig. 7 highlights the strain–stress curve of the nanohelix under compression. The average C–C distance between the edges of two adjacent helix units in the carbon nanohelix is 5.1 Å which is the maximum displacement allowing adjacent helical units to move relatively without overlapping each other. When the compressive strain reaches 1.8% or the nanohelix has compressive displacement 3.88 Å along the axial direction, the nanohelix shows...
uniform and smooth deformation with Young’s modulus 750 GPa close to that of the carbon nanotube and much greater than the modulus of the same nanohelix under tension, suggesting that the carbon nanohelix behaves like an undeformed spring with outstanding extensibility but notorious compressibility. After the deformation strain of the nanohelix goes beyond point A on the SS curve, the adjacent helical units initiate to overlap each other in the circumference direction of the nanohelix, rendering the out-of-axial deformation of the nanohelix accessible. As strain goes up, several abrupt declines of the stress at points B, C, and E are accompanied by the overlap of adjacent helical units and out-of-axial deformation of the helical structure. Eventually, the compressive stress of the carbon nanohelix reaches a plateau with a catastrophic failure of the structure due to the overall buckling effect. The maximum compressive stress with a stable structure is 25 GPa, which pales in comparison with the yield strength under tension. It should be emphasized that the failure stress with compression is the value at the time when the integrity of the structure breaks down, not the material of the nanohelix. These unprecedented findings demonstrate that the carbon nanohelix structure has unique mechanical properties, which provide novel insights into the structure–property relationship of nanostructures, offering a promising way to tailor the mechanical properties of nanostructures with demand, and fuel the exploration of its potential application in multiple areas.

3.4. Molecule packing

Further, we extended our work to studying the potential application of the carbon nanohelix such as molecule storage. Here we propose an intriguing example of the carbon nanohelix implication for water molecule packing and storage shown in Fig. 8. For the
purpose of illustration, water molecule is defined in red colour. The water molecules on the surface of the graphene nanoribbon are modeled as TIP3P, which consists of Coulomb potential between the partial charges on the oxygen (−0.834e) and hydrogen (1.008e) and Lennard-Jones interaction with epsilon(O–O) = 0.152 kJ mol−1, epsilon(O–H) = 0.0836 kJ mol−1, epsilon(H–H) = 0.046 kJ mol−1, sigma(O–O) = 3.1507 Å, sigma(O–H) = 1.7753 Å, sigma(H–H) = 0.4 Å. The interactions between the C–O and C–H are described by Lennard-Jones with epsilon(C–O) = 0.389 kJ mol−1, sigma(C–O) = 3.28 Å, epsilon(C–H) = 0.129 kJ mol−1, sigma(C–O) = 2.81 Å. NVT ensemble with temperature 300 K and the periodic boundary conditions are applied to the system of molecular packing. Based on molecular dynamic simulation, the whole system is eventually packed into the carbon nanohelix and the water molecules form an intriguing helical order due to the vdw interaction with helical graphene sheet and hydrogen bonding interaction between the adjacent water molecules, which is quite different from the phenomena observed in the simulation of water transportation via carbon nanotubes by Nicholls et al.27 The scrolling-up of the carbon nanohelix makes the water molecule compact and acts as a dynamically formed and helical channel to deliver the water molecules. The water molecules fail to leak outside of the helix due to the small intervals between the helix units. The interaction between water molecules and graphene sheet also accelerate the formation of helical graphene structure. The findings here provide guidance into utilizing this promising carbon nanohelix to pack up small molecules and reserve them inside it for potential application such as energy storage and drug delivery.

4. Conclusions

In this paper, we performed molecular mechanics/dynamics simulations to scroll the single graphene sheet into a novel carbon nanohelix structure with a specific hydrogenation pattern and investigate its thermal and mechanical properties to fully reveal potential applications. The findings have demonstrated that the radius and length of the helix unit of the carbon nanohelix heavily depend on the chirality of the graphene nanoribbon. Graphene nanoribbons with high chirality suffer from intense energy barrier to trigger the scrolling up process of generating the carbon nanohelix. Also the carbon nanohelix possesses outstanding thermal stability as well as the amazing mechanical properties, which can be perceived as a representative signature to distinguish itself from the behavior of the carbon nanotube and graphene. The findings provide the guideline of the fabrication and characterization of 3D carbon nanohelix from the experimental prospective as well as further explore its potential applications in nanocomposites, energy storage, and drug delivery vehicles.

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