The tubular conical helix of graphitic boron nitride

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Abstract. We employed a novel synthetic route for the generation of a boron nitride (BN) filamentary nanostructure. A pre-formed filamentary microstructure was used as a template instead of a conventional metal catalyst. BN nanotubes exhibiting the geometry of an Archimedes spiral were obtained via a post-heating process at temperatures above 1750 °C on the intermediate BN microstructures pre-formed under heating to 1700 °C. An enthalpy was found to primarily determine the structures of the resultant helical-conical nanotubes (HCNTs). Therefore, the structural parameters, particularly the apex angles of the cones, can be easily varied via simple annealing. This unique structural property is favourable to interlayer sliding in the HCNT structure, as was documented during electron beam induced deformation. HCNTs can be bent by an angle as high as 180° at room temperature and, then, fully recover the starting morphology after the release of an external stress, exhibiting a spring-like behaviour. The striking elasticity and flexibility of these nanotubes stem from both the high stiffness and the extraordinary flexibility of the BN filaments, and the ease of interlayer sliding in a graphitic structure. The novel BN tubular geometry broadens the range of known helical cone structures. Structural models were developed taking into account the disclination angles or apex angles, wrapping modes, coincidence site lattices and packing patterns of the BN HCNTs.

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1. Introduction

Graphitic filaments can curve to form many interesting structures such as fullerenes, cylindrical nanotubes and cones. The carbon nanotube (CNT) [1] is perhaps the most intriguing nanomaterial and has been proven to possess unique physicochemical properties and have highly promising application potential. To date, CNTs have had the largest known stiffness and bending flexibility among all materials on the Earth [2]–[9]. Molecular dynamics simulations of tube deformation indicate a bond-rotation defect caused by the accumulation of elastic stress, resulting in high resistance to fracture for CNTs [10]–[12].

Typically, one-dimensional graphitic nanomaterials are produced on a metal template. For example, transition metals such as Fe, Co and Ni are the most effective catalysts for the growth of CNTs, or boron nitride (BN) nanotubes, a structural analogue of CNTs [13]–[16]. Our recent study attributed this formation kinetics to the perfect lattice coherence between the transition metal templates and graphitic filaments along some specific directions [17]. Epitaxial crystallization of Co nanorods inside BN nanotubes has been observed, that showed a certain \{011\} plane of cubic Co coinciding with a BN filament with an orientation relationship described by \(\langle 011\rangle_{Co} \parallel \langle 1210\rangle_{BN}\) and \(\langle 455\rangle_{Co} \parallel \langle 01\rangle_{BN}\). Here, we find that a graphitic nanostructure can also be formed on a pre-formed graphitic microstructure. A novel tubular form of BN, displaying the geometry of a hollow conical helix (HCH) or an Archimedes spiral, has been created by this novel synthesis route. There being helical cones rather than stacked cones suggests that the prepared structure consists of a single filamentary belt wrapping in a conical shape. Such geometry allows the nanotube to retain continuity even if the monolayer cones are detached, revealing a spring-like morphology and behaviour.

The discovery of helical–conical nanotubes (HCNTs) broadens the range of known structures of helical cones. In this paper, we first develop complete structural models for HCHs and examine the structures taking into account disclination angles or apex angles, wrapping modes, coincidence site lattices (CSLs) and interlayer packing patterns. Then, the formation mechanism of HCNTs is discussed, highlighting a novel synthesis kinetics occurring during the generation of filamentary nanomaterials. A unique structural property is established for HCNTs,
i.e. transformation of apex angles via simple annealing. An interlayer slide is further favoured in this tubular geometry due to the poor crystallinity along the filament normal; this governs an unusual reversible deformation during electron beam irradiation at room temperature.

2. Experimental details

2.1. BN HCNT synthesis

First, we prepared a BN microstructure via a substitution reaction from CNTs which reacted with B$_2$O$_3$ in a N$_2$ atmosphere [18]. Then, a post-heating process at an increased temperature was carried out for the production of BN HCNTs. CNTs were prepared from a starting mixture of N$_2$ (99.999%), H$_2$ (99.999%) and CH$_4$ (99.9%) by plasma-assisted hot filament chemical vapour deposition (CVD) onto a Ti plate sputtered with Co nanoparticles. The substrate temperature was approximately 773 K. Then, the CNT powder obtained underwent a redox reaction with B$_2$O$_3$ in a N$_2$ atmosphere inside a cylinder graphite crucible in a high frequency (21 kHz) induction furnace JHF-VFX 110 QZ (JEOL). The B$_2$O$_3$ powder was placed at the bottom of the crucible, whereas CNTs were mounted ∼0.8 cm above the B$_2$O$_3$ powders. The B$_2$O$_3$/CNT weight ratio in the starting powders was not less than 7:1. The material was first heated at a temperature of approximately 1700 ºC for 30 min. Then, post-heating at a higher temperature (e.g. 1750 ºC for the specimen S1750 and 1800 ºC for the specimen S1800) was performed for 60 min. The reaction chamber was finally cooled down to room temperature within 90 min in flowing N$_2$.

2.2. Annealing processes

Annealing was performed in order to examine the specific structural properties of the BN HCNTs. After post-heating at 1800 ºC for 60 min, as described above for the specimen S1800, the material was annealed at a decreased temperature in an Ar atmosphere for 30 min. Two annealing temperatures (1700 and 1600 ºC) were adopted in this study.

2.3. Chemical analysis and TEM examination

The x-ray diffraction (XRD) data were collected with a powder diffractometer (Rigaku Rint 2000S) using graphite-monochromatized Cu Kα radiation (λ = 0.15405 nm). The microstructural analysis including the measurements of the apex angles was carried out using a scanning electron microscope (SEM, JSM-6700F) and a 300 kV field-emission transmission electron microscope (TEM, JEOL-3000F). Chemical compositions were acquired by using electron energy loss spectra (EELS) taken on a Gatan DigiPEELS 766 parallel detection spectrometer. In situ TEM observation of HCNT deformation was performed in a JEOL-3000F.

3. Results and discussion

A tubular form of BN was obtained via the present synthesis route, as clearly seen in the TEM micrograph (figure 1(a)). XRD and chemical analysis by EELS reveal a pure graphite-like BN phase with the lattice parameters $a = 0.2502$ nm and $c = 0.3333$ nm. The lattice image (inset in figure 1(a)) displays oblique graphene planes with respect to the tube axis. The electron
Figure 1. (a) A TEM image of a novel BN tubular form, displaying a hollow cone morphology, as confirmed by the diffraction pattern (b); (c) the structural model of a HCNT.

diffraction pattern (figure 1(b)) is in a good agreement with the reported conical structure [19]–[25], which consists of two rows of 00l reflections meeting at an angle equal to 180° − θ_{apex} and hkl arcs along the direction perpendicular to the cone axis. We measured the apex angles of cones in diffraction patterns when the cone axis was roughly perpendicular to the incident beam. The diagram in figure 2 indicates a narrow distribution of the apex angles, each of which coincides with the theoretical value corresponding to a certain disclination configuration [20, 26]. It is seen that
Figure 3. The disclination operation of $\theta_D = 120^\circ$ around a sixfold axis (left in (a)) and a threefold axis (right in (a)). The former gives a square at the apex of a cone (b) while the latter (c) shows an apical atomic configuration of either a single-bridged atom (d) or a pentagon-dipole (e) defect.

the majority of disclination angles include $\theta_{\text{over}}$ in addition to $n60^\circ$, indicative of a helical nature rather than a stacked cone nature for the present BN HCNTs (for details, see the next section). The BN nanotubes obtained were therefore formed via wrapping a narrow BN filamentary belt, employing the geometry of an Archimedes spiral, as illustrated in figure 1(c). A tubular conical helix is then obtained via the present synthesis kinetics. The observed disclination angles at $180^\circ$ and $240^\circ$ (figure 2) may relate to either helical or non-helical cone structure, which could not be distinguished by the techniques available. For the present BN HCNTs, only $\theta_{\text{over}} = 21.8^\circ$, $27.8^\circ$ and $13.2^\circ$ were observed. These three values correspond to three CSLs with the lattice parameters of $\sqrt{7}$, $\sqrt{13}$ and $\sqrt{19}a_0$ ($a_0$ refers to the in-plane dimension of the h-BN unit cell), respectively [26]. They are the three smallest CSLs, indicative of an actual configuration with high densities of coincidence lattice sites (CLSSs) between overlapping layers.

HCH geometry broadens the range of known helical cone structures. First, let us thoroughly examine the structures of a novel filamentary conical helix.

3.1. Structures

A cone can be obtained through an operation during which a sector of angle $\theta_D$ (the disclination angle) is removed from a flat graphitic-like sheet. The two cut sides of the sheet are joined

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together to form a sealed monolayer cone (figure 3(a)); or unsealed monolayer cones stack on top of each other and interconnect in a helical fashion via a single screw dislocation. For a sealed monolayer cone or a stacked (non-helical) cone, owing to the hexagonal symmetry of the graphitic structure, continuity at the junction upon buckling of the sheet following the disclination operation is only satisfied if $\theta_D$ takes the form of multiples ($n$) of $60^\circ$ [19, 20]. A single $(6 - n)$-membered ring defect is generated at the conical apex. For example, a square is formed for a disclination of $\theta_D = 120^\circ$ ($n = 2$) (figure 3(b)). For C cones, $n$ can take any integer value from one to five. However, in BN, even-membered rings and, in particular, squares are thought to be the preferred defects because they do not need the inclusion of B–B or N–N bonds, which are weaker than the B–N bonds [25]. Contrary to a critical selection criterion for the disclination angles of non-helical cones, helical cones show broader disclination configurations due to the possible introduction of an additional overlap angle ($\theta_{\text{over}}$) in $\theta_D$, i.e. both $\theta_D = n60^\circ$ and $n60^\circ \pm \theta_{\text{over}}$. The overlap angles were found to display specific values (e.g. 13.2$^\circ$, 21.8$^\circ$ and 27.8$^\circ$), which are attributed to the formation of high densities of CLSs between the overlapping layers [19]–[22]. The CSL provides a certain magnitude of interlayer forces, which guarantees the formation of such curved structures.

So far, cone structures (helical and non-helical) have been examined exclusively in the light of wrapping the filament around a $60^\circ$ (sixfold) symmetry position, i.e. the centre of a hexagon in a honeycomb sheet (figure 3(a)) [19]–[25]. This is based on the consideration of a stable topological defect (two- to five-membered rings) at the conical apex (figure 3(b)). Wrapping the filament around a $120^\circ$ (threefold) symmetry position, i.e. an individual atom, has been considered unfavourable because it will introduce a highly strained apex. For example, a $\theta_D = 120^\circ$ disclination operation around a threefold axis will generate either a single-bridged atom or a pentagon-dipole at the conical apex (see figures 3(c)–(e)). Such a highly distorted cluster is energetically unfavourable and cannot occur or serve as a nucleus for a cone. Owing to this consideration, no report has ever been available on the cone structures formed via wrapping around a threefold axis. However, the present observation of a filamentary HCH geometry shows a continuous interior channel where the conical apexes were removed. The otherwise unstable apex in a cone via wrapping around a threefold axis does not exist in HCH, which allows us to consider the possible existence of wrapping modes around both sixfold and threefold axes. It is emphasized here that the BN HCNTs were formed via wrapping a filamentary belt onto the curved surface of an intermediate BN filamentary microstructure, as described below. This formation kinetics avoids the occurrence of cone apexes. Here, we establish complete structural models (see table 1) for helical cones by taking into account the wrapping modes, disclination angles (or apex angles), CSLs and packing patterns.

It is found that the size of a CSL is determined by $\theta_{\text{over}}$, whereas the packing pattern of a CLS is dominated by the wrapping modes and $n$ [26]. The sixfold wrapping can display atom-on-atom (at $\wedge$ at) and channel-on-channel (ch $\wedge$ ch) packed CLSs, while an additional at $\wedge$ ch case takes place within the CLS configuration via wrapping around a threefold axis. For a $\theta_D = n60^\circ$ disclination, where $\theta_{\text{over}} = 0$, the CSL has identical lattice dimensions to the graphitic structure. When wrapping is performed around a sixfold axis, each turn of the helix could bring successive layers back into exact coincidence. The packing of overlapping layers could be of either AA′AA′ or AAAA type, which are governed by an odd or even $n$, respectively. For BN, AA′AA′ stacking is energetically more favourable than AAAA stacking, since the former allows B (N) atoms to stack onto N (B) atoms, whereas the latter represents the packing of the same element over itself. In any case, both of the stacking patterns are unfavourable for C helical cones. A favoured packing
Table 1. Disclination configurations and CSL structures. ($a_0$ represents the basic in-plane lattice parameter of graphitic structure.)

| Disclination angles | CSL type and lattice parameter (units of $a_0$) | CSL stacking patterns |
|---------------------|-----------------------------------------------|----------------------|
| $(2k + 1)60^\circ$  | 6-fold BN-type                                 | AA′AA′               |
|                     | 3-fold Graphite-type                           | ABAB                 |
| $2k60^\circ$        | $\Sigma 7$                                    | AAAA                 |
| $n60^\circ \pm 21.8^\circ$ | $\sqrt{7}$                                    | AAAA                 |
|                     | $\Sigma 19$                                    | AA′AA′ $n = 2k$      |
|                     | $\sqrt{19}$                                    | at $\wedge$ at       |
| $n60^\circ \pm 13.2^\circ$ | $\Sigma 37$                                   | AAAA $n = 2k + 1$   |
|                     | $\sqrt{37}$                                    | ch $\wedge$ ch       |
| $n60^\circ \pm 27.8^\circ$ | $\Sigma 13$                                   | AAAA                 |
|                     | $\sqrt{13}$                                    | at $\wedge$ at       |
| $n60^\circ \pm 17.9^\circ$ | $\Sigma 31$                                   | AA′AA′ $n = 2k + 1$  |
|                     | $\sqrt{31}$                                    | at $\wedge$ at       |
| $n60^\circ \pm 15.2^\circ$ | $\Sigma 43$                                   | AAAA $n = 2k$        |
|                     | $\sqrt{43}$                                    | ch $\wedge$ ch       |

pattern for C showing an ABAB sequence is obtained via wrapping a $(2k + 1)60^\circ$ disclinated filament around a threefold axis. Figures 4(a) and (b), for example, show the packing structures of overlapping layers for a disclination angle of $180^\circ$, which evidences the dominant role of the wrapping mode in the structures of helical cones.

If an additional $\theta_{\text{over}}$ is combined with $n60^\circ$ during the disclination operation, the helical cones formed can be classified into two groups (table 1), each of which shows a certain law of structural dependence on the wrapping modes and $n$. Table 1 lists six small CSLs and corresponding disclination angles. Among those additional overlap angles, the two smallest CSLs form when $\theta_{\text{over}} = 21.8^\circ$ and $27.8^\circ$. They show CSL lattice parameters of $\sqrt{7}$ and $\sqrt{13}$ and are, hence, denoted as $\Sigma 7$ and $\Sigma 13$ CSLs, respectively [26]. These two overlap angles have been frequently observed in graphitic conical helices. CSLs with the larger lattice parameters have also been observed experimentally, though not frequently. In the case of rotation around a sixfold axis, CLSs could only be of the at $\wedge$ at and ch $\wedge$ ch types, whereas they may be either of at $\wedge$ at and ch $\wedge$ ch types or at $\wedge$ at and at $\wedge$ ch types for the rotation around a threefold axis. However, the at $\wedge$ at coincidence sites show different packing sequences for the two rotation
Figure 4. Structural models of helical cones: (a), (b) with a $\theta_D = 180^\circ$ disclination; (c), (d) with a $\theta_D = 120^\circ - 21.8^\circ$ disclination. The cones in (a) and (c) are formed via wrapping around a sixfold axis, while those in (b) and (d) are formed via wrapping around a threefold axis. Note the inverse handedness of rotation in (a) and (b).

modes. Rotation around a threefold axis has exclusively the AAAA stacking, while both AAAA and AA′AA′ sequences may appear in CSLs, while rotating around a sixfold axis. Figures 4(c) and (d) depict the $\Sigma 7$ CSLs with a disclination of $120^\circ - 21.8^\circ$ for rotation around the sixfold and threefold axes, respectively.

The experimental observation detects a narrow distribution of the apex angles, which, for example, in the specimen S1800, is peaked at $\sim 52^\circ$ and, hence, the disclination angle of $180^\circ + 21.8^\circ$ (figure 2). It can be seen from table 1 that this disclination angle leads to the CSL configuration displaying CLSs of the ch $\wedge$ ch-type and unfavourable AAAA-type at $\wedge$ at packing, regardless of the rotation mode. Keeping in mind a disclination angle of $180^\circ + 27.8^\circ$, which is close to $180^\circ + 21.8^\circ$, we obtain a favourable AA′AA′-type at $\wedge$ at packing although the size of the CSL increases from $\sqrt{7}$ to $\sqrt{13}$. The fact that $180^\circ + 21.8^\circ$ disclination is dominant in the S1800 specimen implies that the size of the CSL and, hence, the density of CLSs are the dominant factors determining the configuration of a conical helix rather than the stacking sequences. This is different from the case for the BN graphitic plates which ‘prefer’ AA′AA′ rather than AAAA packing. In HCH, the highly curved filaments could only be stabilized via interlayer van der Waals forces, which are determined by both the CSL and the packing pattern, i.e. the density of interlayer interactions and the type of interaction. It appears that a high density of interactions of the weak B–B and/or N–N type gives rise to the stronger interlayer bonding than a low density of interactions of the strong B–N type. Anyway, the synthesis temperatures determine the size and the apex angle (and thus the bending curvature and CSLs) of the resultant conical helices.

The structure of a perfect conical helix is totally determined by four elements: the disclination angle (or apex angle), the wrapping mode (about the symmetrical position), the
radius/wall thickness and the handedness of the rotation. The first two elements dominate the packing pattern for overlapping layers and the structure and size of the CSL, as fully documented above. Radius and tubular wall thickness are the parameters determining the morphology of HCHs. Handedness of the rotation is the most important structural parameter; it refers to the wrapping of a filamentary belt in the right-handed (e.g. figure 4(a)) or left-handed (e.g. figure 4(b)) fashion. Thus, the as-obtained conical helices with respect to these two wrapping fashions are related by a mirror reflection. Inversion in handedness of rotation could possibly result in a complete change in properties; this has been widely documented in organic chemistry. Therefore, both theoretical and experimental work is required to evaluate the relation between the structural parameters and physicochemical properties of HCH. Above all, it is especially demanding to find effective and convincing ways to characterize and, if possible, control the wrapping modes and handedness of rotation for a HCH.

3.2. Formation mechanism

BN HCNTs could only be obtained when significant excess of B$_2$O$_3$ in the starting powder mixture (high B$_2$O$_3$/CNTs ratios) and high post-heating temperatures were employed. Reaction at 1700 °C (specimen SH1700) was found to form a new BN microstructure, as shown in figure 5(a), which displays morphology similar to bamboo-like fibres, albeit with a uniform curvature and a short spacing between neighbouring compartments. The curved surfaces of ‘microworms’ have been found to serve as templates for the nucleation and growth of HCNTs, as evidenced in figure 5(b). Therefore, the chemical reactions during the formation of BN HCNTs can be described as follows [27].

At 1700 °C (heating stage):

$$3\text{C (nanotubes)} + 2\text{B}_2\text{O}_3 + 2\text{N}_2 \rightarrow 4\text{BN (‘microworms’)} + 3\text{CO}_2.$$  

At 1750 or 1800 °C (post-heating stage):

$$\begin{align*}
\text{C (crucible)} + \text{B}_2\text{O}_3 & \rightarrow 2\text{BO} + \text{CO} \\
\text{B}_2\text{O}_3 + 3\text{CO} + \text{N}_2 & \rightarrow 2\text{BN (HCNT)} + 3\text{CO}_2 \\
6\text{BO} + \text{N}_2 & \rightarrow 2\text{B}_2\text{O}_3 + 2\text{BN (HCNT)} \\
\text{BN (‘microworms’)} & \rightarrow \text{BN (particles)}.
\end{align*}$$

Previous work on C → BN nanotube conversion has documented that CNTs act as both templates and reduction reagents during the formation of BN nanostructures [28]. Since all CNTs were consumed during the first heating stage in the present work, as confirmed by the chemical analysis of the specimen SH1700, the reduction reagent for the reactions during the post-heating stage may only appear in accord with the reaction (2), i.e. a CO vapour originates from the graphite crucible used. Therefore, CNTs played no role in the formation of nanostructures during the post-heating stage. The possible contribution of metal particles to the nucleation of conical nanotubes, as observed in bamboo-like nanofibres by several authors [29]–[33], is ruled out due to the absence of Co crystallites at the HCNT ends. On the other hand, the curved surfaces of the ‘microworms’ could be responsible for the formation of conical graphitic sheets rather

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than cylindrical tubules (see figure 5(b)). Since fewer BN ‘microworms’ were observed in the final HCNT specimens, most of the thin ‘microworms’ were eventually collapsed and converted to particles at the later stage of post-heating at temperatures over 1750 °C (see reaction (5)). Then, the formation mechanism of BN HCNTs can be clarified, as depicted in figure 5(c). It is possible that the nucleation of HCNTs on the surface of the ‘microworm’ leads to a disclination configuration depending on the curvature of the ‘microworms’ and the cone size. The absence of polygon defects results in a conical appearance rather than fullerene-type shells packed onto the curved surface of ‘microworms’. The HCNT growth kinetics observed here suggests a novel way for generating filamentary nanostructures. The pre-existing filamentary microstructure can serve as a template in place of a conventional metal catalyst particle.

It has been indicated that an enthalpy ($\Delta H$) is the driving force for the formation of curved structures, whereas an entropy ($\Delta S$) plays a dominating role in the distribution of the disclinations.
formed [22]. In the previous nucleation and growth models for solid cones or bamboo-like fibres on catalysts, the disclination configuration was determined during the nucleation stage and does not change after seeding [19]–[22], [29]–[33]. However, the absence of apexes and catalytic particles at the tube ends, along with the narrow distribution of apex angles and, therefore, disclination angles, as observed in BN HCNTs, contradicts the assertion of a dominant role for the entropy in the present case. The S1800 and S1750 specimens post-heated at different temperatures show different distributions of apex angles (figure 2), though they had experienced the same heating temperature (1700 °C) at which ‘microworms’ were generated. This excludes the possibility of a dependence of the final apex angles on the curvature of ‘microworms’. These results imply changes of disclination configuration during the post-heating process, which transforms the apex angles to a stable value determined by the temperature (figure 5(c)). Thus, the single enthalpy factor determines the final disclination configuration of HCNTs. Change of the disclination configuration and, hence, the apex angle was also observed during an annealing process described below.

3.3. Structural properties

In the present work a sole thermodynamic element, enthalpy, was proved to determine the final structures including apex angles of HCNTs. This phenomenon implies an interesting structural property, i.e. transformation of apex angles via annealing. In other words, we can control the apex angle, the most important structural parameter within the present conical geometry. Therefore, annealing processes at two different lowered temperatures (1700 °C for specimen SA1700 and 1600 °C for specimen SA1600) were performed. The two annealed specimens, as found by TEM analysis, show simultaneous reduction of the apex angles but increase in the tubular radius as the annealing temperature decreases. Table 2 summarizes the measured apex angles and $R_{av}$ (an average tubular radius, $R_{av} = (R_{in} + R_{ex})/2$, where $R_{in}$ and $R_{ex}$ represent interior and exterior tubular radii, respectively) for SA1700 and SA1600. For comparison, the measured structural parameters for the specimens S1800 and S1750 are also presented in table 2. It is seen that the peaked apex angle tends to be 35° and 30° for the specimens SA1700 and SA1600, respectively. The smallest apex angle was observed in SA1600, displaying a value of 19°, corresponding to the highest disclination angle of 300°. Such small apex angles cannot be obtained via a single heating/post-heating procedure. Annealing allows us to obtain HCNTs with even smaller apex angles, if further decrease in annealing temperature is effected. Then, an artificial control of the structures and, hence, the properties becomes possible for this specific tubular geometry. It is noted that the reconstructed conical configuration after annealing also involves ordered stacking modes showing specific values of $\theta_{over}$.

It has been indicated that the strain energy within a curved filament is proportional to the bending curvature. Then, a high strain arising from filament bending to form the conical helix can be relaxed via annealing at low temperatures, which leads to increase in radius and decrease in bending curvature. In any case, systematic reduction of apex angles with decrease in annealing temperatures is most valuable. The implication is that this important structural parameter can be under precise control. The estimation of strain energy [27] for HCNTs according to Tibbetts [34] and Robertson et al [35] reveals a synchronous change of strain energy with apex angle. Thus, a small $\theta_{apex}$ is energetically more favourable for a given $R_{av}$. It is noted that large apex angle relates to large curvature difference (characterized by $\sin(\theta_{apex}/2)$) on the curved filament. A large curvature difference indicates higher density and larger variety of distorted bonds in a
given structure, leading to a lack of structural rigidity, periodicity and continuity, i.e. higher strain energy, which destabilizes the structure. Only high temperature, i.e. enthalpy, can provide energetic support for the formation of such severely strained structure at the expense of the crystal potential. Strain relaxation is achieved by decreasing the apex angles in addition to increasing the tubular radius. Reconstruction of the molecular structure can be performed via filament slide and, possibly, through skipping of atoms within a certain range, leading to a configuration with a decreased overall bending curvature and a moderate curvature difference. The least strained curved geometry is expected to be achieved when $\theta_{\text{apex}}/2 = 0$, i.e. for the conventional cylindrical nanotubes. This accounts for the fact that cylindrical BN nanotubes were usually obtained at relatively low temperatures, e.g. 1200–1500°C, whereas the higher temperatures (>1750°C) generated conical structures [23, 24].

3.4. Deformation

The as-observed structural property, which relies on changes of apex angles via annealing, implies a more favourable interlayer slide in this specific HCH structure. It is known that the
shear modulus of graphite (4.5 GPa) is smaller than its Young’s modulus (1 TPa). Therefore, it is much easier to slide the filaments than break them [36, 37]. The weakened interaction forces between the overlapping layers in HCNTs due to the poor crystallinity normal to the sheet plane (noting that the smallest $\Sigma 7$ CSL is still $\sqrt{7}$ times larger than the h-BN unit cell [26] and weak AAAA-type at at CLSs may occur) further favour sliding due to thermal treatment. Similarly, one can expect the same transformation process triggered by an exterior stress. This was indeed observed by us during an in situ TEM study at room temperature. Figures 6(a)–(d) display the morphological changes of an individual BN HCNT bearing a deformation induced by an electron beam. The current density of the electron beam first increased rapidly from 90 (figure 6(a)) to 140 pA cm$^{-2}$ (figure 6(b)) and, then, to 160 pA cm$^{-2}$ (figure 6(c)) and finally decreased to 90 pA cm$^{-2}$ (figure 6(d)). The bending behaviour of the BN HCNT effected via changing the electron beam intensity could be originating from either electrostatic forces or charging effects in insulating materials [38]. By monitoring the sites of the nanotube labelled $a$, $b$, $c$ and $d$ in figure 6, the change in shape during deformation can easily be recognized. Importantly, bending to larger angles than those peculiar to any other inorganic material is visible. Our recent work has indicated that HCNTs can be bent by a maximum angle as high as 180° [39]. By comparing figure 6(a) with figure 6(d), we find that the nanotube recovers the starting morphology soon after the release of the exterior stress and exhibits no evidence of structural failure. Therefore, a spring-like behaviour is evidenced for HCNTs.

Deformation of HCNTs is solely determined by the crystallographic factors since only rotation and/or slide of filaments are involved in the deformation owing to the specific geometry of HCNTs. This is due to the fact that bending, stretching, twisting and even a compressive stress normal to the tube axis contain a shear along certain cone surfaces. Recently, we have established deformation models for HCNTs [39]. Figure 7 illustrates how a HCNT changes its geometry during torsion and tension. Bending could be regarded as integration of the separate tension or compression modes for each monolayer cone within the HCH structure. In figure 7, it is seen that the number of monolayer sheets along the tube axis increases during twisting in accordance with the wrapping direction. Meanwhile, the apex angle and tubular radius decrease, leading to increase in the tube length. Torsion maintains perfect conical helix structure without additional stress induced strain. The CSL configuration is maintained, though the size of the CSL could be changed. During tension, the number of wrapping layers remains constant. Then, there has to be a reduction in apex angle along with an increase in length and a decrease in radius. However, the local bonding structure could be distorted. The higher strain is observed at the top
of each conical fragment, as indicated by arrows in figure 7. The innermost walls bear the larger strain during tension, which is inversely proportional to the interior radius. It can be seen that topological defects are not necessarily introduced during the deformation of a HCNT which is performed solely by sliding of filaments. For a HCNT with large interior radius, only extreme tension will lead to initiation of topological defects, such as double pentagon–heptagon defect pairs, which originate on the innermost walls. Such a situation will arise when the deformed HCNT reaches a close-to-zero apex angle and an extreme length that could be tens to hundreds times the starting tube length. Geometrical consideration shows that torsion leads to a faster change in length than tension does, but to slower modification of the apex angle, as seen in figure 8.

Electron beam induced deformation leads to unexpected modification of the tubular shape, which may involve any of the deformation processes including twisting, stretching, compressing and bending. Nevertheless, all of them proceed along with changes in apex angles [39]. It can be seen in figure 7 that torsion and tension result in decreases in the tubular radius and overlapping area and, hence increase the strain energy and weaken the interlayer interactions. A HCNT with such an unstable structural configuration will clearly soon recover the previous stable geometry after the exterior stress is released. Again, only filament slide is involved in the structural recovery, though in the opposite direction. A typical spring-like behaviour occurs. The actual spring-like geometry of the HCNT is believed to derive advantage from both the high stiffness and extraordinary flexibility of BN filaments and the ease of interlayer sliding in graphitic structure, thus leading to remarkable endurance under high strains and strong resistance to fracture.

The as-observed deformation behaviour suggests striking flexibility and elasticity in HCNTs, comparable to those of metals. Together with the inherent high strength and outstanding chemical and thermal stability, BN HCNTs show, in many respects, clear advantages over metal, polymer and inorganic compound nanofibres and may become key candidates for applications in high performance composite materials. The structural properties of HCNTs observed here suggest a rare possibility to control apex angles artificially. Though the exact role of the apex angle in physicochemical properties, e.g. field emission and hydrogen storage, of HCNTs is as yet unclear, the present discovery suggests the experimental possibility of finding a relationship between apex angles and properties. Further theoretical and experimental work is required to investigate the role of complex structural parameters, e.g. apex angles, handedness of rotation and CSLs, in physicochemical properties of BN HCNTs.
4. Summary

We synthesized a novel tubular form of boron nitride, exhibiting a tubular conical helix geometry, on pre-formed BN ‘microworm’ structure. Complete structural models were established for helical cones taking into account the disclination angles or apex angles, wrapping modes, CSL, packing patterns and handedness of rotation. A sole dynamic element, i.e. enthalpy ($\Delta H$), was found to determine the disclination configuration of HCNTs. The specific geometry of HCNTs leads to an interesting structural property, i.e. transformation of apex angles via annealing; this indicates a possible structure design and smart control of the material properties. In addition, this unique structural property leads to a reversible deformation of the HCNT, which was observed during in situ TEM electron beam irradiation at room temperature. HCNTs can bear extremely severe strain without any evidence of structural collapse or fracture. Moreover, they can recover the previous morphology as soon as the exterior stress is released, displaying a unique spring-like behaviour. The remarkable flexibility and elasticity in HCNTs indicate promise for potential applications in new-generation high performance composite materials.

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