

The Deformations of Carbon Nanotubes under Cutting

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Supporting Information

ABSTRACT: The determination of structural evolution at the atomic level is essential to understanding the intrinsic physics and chemistries of nanomaterials. Mechanochemistry represents a promising method to trace structural evolution, but conventional mechanical tension generates random breaking points, which makes it unavailable for effective analysis. It remains difficult to find an appropriate model to study shear deformations. Here, we synthesize high-modulus carbon nanotubes that can be cut precisely,



and the structural evolution is efficiently investigated through a combination of geometry phase analysis and first-principles calculations. The lattice fluctuation depends on the anisotropy, chirality, curvature, and slicing rate. The strain distribution further reveals a plastic breaking mechanism for the conjugated carbon atoms under cutting. The resulting sliced carbon nanotubes with controllable sizes and open ends are promising for various applications, for example, as an anode material for lithium-ion batteries.

KEYWORDS: carbon nanotube, structural deformation, shear, anisotropy

arbon nanomaterials such as carbon nanotubes exhibit a unique conjugated structure of carbon atoms. Thus, they have been widely explored for next-generation electronics,^{1,2} in particular, flexible electronic devices. An atomic-level understanding of their structural evolution under deformation is critical for utilizing their mechanical,^{3–7} electronic,^{8,9} and optical properties.^{10,11} Mechanochemistry represents a promising method for studying structural evolution.¹²⁻¹⁴ Generally, a nanoscaled object or a molecule is stabilized at one end by a substrate, while the other end is pulled to break it. For instance, carbon nanotubes have been pulled to elongate and break along the length direction.^{15–17} However, the difficulty of controlling the breaking point hinders more effective analysis. Alternatively, a shear force can be accurately applied at a specific position of an object to deform it; however, a shear force is rarely used to break nanomaterials because of the difficulty in precision cutting and rational analyzing structural evolution using currently available technologies.^{18,1}

Here, we study the structural evolution of conjugated carbon atoms by synthesizing tailorable multiwalled carbon nanotubes (MWCNTs) as an effective model (Figure 1a). Aligned MWCNT arrays were first grown by two-step chemical vapor deposition with different growth temperatures (Methods).¹¹ More specifically, an MWCNT array was first synthesized at 750 °C, and the MWCNTs typically showed a diameter of ~ 8 nm (Figure 1b). These functioned as templates for the continuous growth of graphene layers on their outer surfaces at a higher temperature of 1060 °C. The diameters of the MWCNTs increased to 10-125 nm as the growth time increased to 10-120 min (Figures 1c and S1). Compared with other randomly assembled MWCNTs, the highly aligned MWCNT array is crucial for analyzing the lattice deformations in circular section (Figure 1b). Here, the geometry phase analysis (GPA) method was used to directly measure the deformations at atomic scale, which already proved efficient in evaluating the dislocations in graphene and strain distributions in metallic nanoparticles.^{20,21} A transmission electron microscopy (TEM) image displayed clear crystal lattices, and the corresponding GPA image showed no strain cores, indicating low defects and internal stress (Figure S2).

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Figure 1. Schematic and structural characterization of sliced MWCNTs. (a) Schematic illustration of the slicing process of aligned MWCNTs. (b) Side views of scanning electron microscopy (SEM) image of aligned MWCNTs. Scale bar, 100 μ m. (c) MWCNTs with increasing diameters of 8, 10, 15, 40, and 65 nm (from left to right). Scale bar, 5 nm. (d) SEM image of a layer of sliced MWCNTs. Scale bar, 5 μ m. (e and f) Side views of SEM images of sliced MWCNTs arrays. Scale bar, 3 μ m.



Figure 2. Structural deformations in sliced MWCNTs. (a) Cross-sectional TEM images of MWCNTs sliced perpendicularly at speeds of 1, 5, 10, and 20 mm/s, respectively. Scale bar, 20 nm. (b) Distributions of the ratio of $L_{//}$ and L_{\perp} corresponding to (a) at slicing speeds of 1, 5, 10, and 20 mm/s. $L_{//}$ and L_{\perp} are defined as the distances of the parallel and perpendicular axes relative to the slicing direction in (a), respectively. The $L_{//}/L_{\perp}$ ratio approaches closer to 1 at higher slicing speeds. (c) Dependence of the $L_{//}/L_{\perp}$ ratio on the diameter, for increasing slicing speeds. The diameter is calculated from the square root of $L_{//} \times L_{\perp}$. Larger MWCNTs exhibit lower $L_{//}/L_{\perp}$ ratios at the same slicing speed.

RESULTS AND DISCUSSION

The aligned MWCNTs were cut by a diamond knife perpendicularly at different rates (Figure 1a and Supporting Information). The MWCNTs could be clearly cut without being pulled out of the array, and both cut sections were smooth (Figure 1d-f). The length of the MWCNT could be accurately controlled from nanometers to micrometers, and a length of 50 nm was used for the following analysis. By



Figure 3. Impact of anisotropy and chirality on structural transformation. (a) Representative cross-sectional TEM image of a MWCNT with the $L_{//}/L_{\perp}$ ratio of 1.10. Scale bar, 5 nm. (b and c) High-resolution TEM images of the marked red and blue boxes in (a), respectively. Scale bar, 2 nm. (d and e) Two-dimensional fast Fourier transform derived from (b) and (c), respectively. (f and g) High-resolution TEM images to show the values of $\delta_{//}$ and δ_{\perp} , respectively. Scale bar, 0.5 nm. (h) Schematic illustration of the evolution of the diameter and lamellar distances parallel and perpendicular to the slicing direction. $\delta_{//}$ and δ_{\perp} correspond to the lamellar distances of the graphene sheet along $L_{//}$ and L_{\perp} , respectively. The difference in chirality at different walls of the MWCNTs causes the graphene layers to be sliced with different symmetries. (i) Dependence of $\delta_{//}/\delta_{\perp}$ on $L_{//}/L_{\perp}$ to demonstrate the contribution of the displacement of graphene layers. (j and k) The distribution of δ in graphite being sliced in perpendicular and parallel directions relative to the conjugated plane. The arrow in each graph indicates the slicing direction.

contrast, conventional MWCNTs could not be cut and were easily pulled out (Figure S3). It is also confirmed that shear stress along the cutting direction and tensile stress along the longitudinal direction coexisted during the slicing process.

MWCNTs typically displayed a perfectly circular crosssection in the initial state. However, this shape was distorted into an elliptical shape along the cutting direction (Figures 2a and S4). The strains remaining in the fractured section after cutting were useful indicators of the structural evolution. The structural evolution is predicted to be influenced by the initial nanostructure (*e.g.*, chirality and diameter) and external parameters (*e.g.*, strain rate).^{22–25}

A systematic study of the structural evolution in the corsssection can be helpful to understand the properties and breaking mechanism. Two key factors, the strain rate and the initial atomic structure (*i.e.*, anisotropy, chirality, and curvature), were carefully studied.

To investigate the impact of the strain rate on the atomic structure of MWCNTs, the MWCNTs were perpendicularly sliced at increasing speeds. The ratios of diameters along $(L_{//})$ and perpendicular (L_{\perp}) to the slicing direction were used to quantitatively compare the extent of the atomic structure evolution. The section shape of the MWCNTs showed greater deviation from the circular shape at a lower slicing speed. With

increasing speeds, the structural deformations gradually decreased, and the cross-section maintained the initial circular shape, as the value of the $L_{//}/L_{\perp}$ ratio approached 1.0 (Figure 2b,c).

For example, when MWCNTs with a diameter of 93 nm were sliced at speeds of 1, 5, 10, and 20 mm/s, the average $L_{//}$ L_{\perp} ratios were calculated as 1.24, 1.09, 1.01, and 1.02, respectively. Similarly, the same rule could be applied to other MWCNTs with different diameters. A systematic study of the impact of the strain rate and diameter on the nanostructural evolution is summarized in Figure 2c. For a constant slicing speed, the strains also varied with the diameter of the MWCNTs. Larger MWCNTs exhibited lower deformations and maintained their original shape because their higher stiffness restricted the generation of plastic yields. Therefore, smaller atomic structural deformations were observed in larger MWCNTs with higher stiffness.

To gain a more detailed understanding of the structural evolution, we examined the atomic structure at different local areas and elucidated the influence of orientation. Here, a strong anisotropy of the initial atomic structure at the local areas was a key factor for the deformation from a circular to an elliptical shape. We selected two local areas for comparison, with conjugation planes parallel and perpendicular to the slicing



Figure 4. Structural model and evolution of atomic lattices under slicing. (a) Schematic illustration of sliced graphene layers (x-y plane) along the z-axis in the x-z plane (type I, zigzag slicing) and y-z plane (type II, armchair slicing). (b and c) Calculated structural snapshots of graphene layers, including shear and tensile strains along the I and II directions under slicing, respectively. (d) Schematic illustration of sliced graphene layers (x-y plane) along the x-axis in the x-z plane (type III, zigzag slicing) and y-axis in the y-z plane (type IV, armchair slicing). (e and f) Calculated structural snapshots of graphene layers, also including shear and tensile strains in the III and IV directions under slicing, respectively. For (b, c, e, and f), the left, middle, and right columns correspond to the original state and the states under deforming and after breaking, respectively.

direction in an MWCNT and with the $L_{//}/L_{\perp}$ ratio of 1.10 (Figure 3a-c). Two-dimensional fast Fourier transform was used to count the distributions of lamellar distances labeled as $\delta_{//}$ and δ_{\perp} in Figure 3a. The average $\delta_{//}$ was calculated as 3.54 Å and was higher than the average value of 3.45 Å for δ_{\perp} (Figure 3d,e). TEM also verified that $\delta_{//}$ was higher than δ_{\perp} (Figure 3f,g). The relatively higher $\delta_{//}$, to some extent, caused the cross-section to distort into an elliptical shape along the slicing direction (Figure 3h,i). The broad distribution of $\delta_{1/2}$ and narrow distribution of δ_{\perp} were verified in the fast Fourier transform images, demonstrating greater displacements in the areas where the graphene layers were sliced perpendicularly. Further experimental results showed that δ_{\perp} values remained almost unchanged, whereas both the $\delta_{//}$ values and the $\delta_{//}/\delta_{\perp}$ ratios increased with increasing $L_{//}/L_{\perp}$ ratio (Figure 3i and Figure S5). Moreover, the deviation of the fitting curve from the reference line indicated that the displacements of the graphene layers were not completely a result of the atomic lattice transformations, and non-negligible distortions of carbon-carbon bonds also existed (Supporting Information).

To verify the assumption that a strong anisotropy of the initial atomic structure caused the disparity in the lattice fluctuations, graphite samples were sliced, and two types of samples, parallel and perpendicular to the slicing direction, were selected to study the distributions of lamellar distances (Figure 3j,k and Supporting Information). The average lamellar distances across ($\delta_{//A}$) and along ($\delta_{\perp A}$) the graphene layers were ~3.61 and ~3.47 Å, respectively. Slicing across the relatively weak $\pi - \pi$ conjugation planes generated larger lattice displacements.

For a better understanding toward the influence of anisotropy and chirality on atomic evolution, first-principles calculations^{23,26,27} were performed (Supporting Information), and structural snapshots were carefully compared during the slicing process, in which there was a coexistence of shear and tensile stresses (Figure 4). On the one hand, when graphene layers (x-y plane) were sliced along the z axis in the zigzag direction (Figure 4b, type I), the lamellar distances increased after the breaking of carbon-carbon bonds. Similar results were obtained for armchair slicing along the z-axis (Figure 4c, type II). By contrast, when graphene layers were zigzag-sliced along the x-axis (Figure 4e, type III) and armchair-sliced along the yaxis (Figure 4f. type IV), δ was only slightly enhanced. More distortions of carbon-carbon bonds were observed for types I and II than III and IV. The slicing direction was critical for atomic rearrangements. On the other hand, the extents of the



Figure 5. Impact of curvature on the strain distribution. (a–i) High-resolution TEM images, corresponding strain maps (e_{xxy} along the slicing direction) and isometric plots of the strain intensity of the sliced cross-sectional areas with average curvatures of 0.021 nm⁻¹ (a–c), 0.042 nm⁻¹ (d–f), and 0.143 nm⁻¹ (g–i), respectively. θ represents the angle between the axial direction of the carbon/carbon bonds and the slicing direction. The color variation indicates the strain values ranging from –1 to 1. Scale bar, 1 nm. (j) Dependence of strain and strain energy on the curvature of the sliced cross-sectional area.

increases of δ for the zigzag and armchair directions were different. Zigzag slicing generated larger displacements of conjugation planes, verifying the influence of chirality on the atomic rearrangements. Compared with anisotropy and chirality, the orientation of atomic lattice predominates the atomic rearrangements, and the chirality may generate small fluctuations. The value of tensile stress generated from slicing process was almost the same as the calculated fracture stress of simply stretching the graphene layers, providing a definite evidence for our slicing process (Supporting Information and Figure S6).

Unlike planar graphite, conjugated carbon atoms in MWCNTs possess a certain amount of curvature. To study the effect of curvature on the distortion of atomic structure, conjugated planes with different curvatures were carefully compared in terms of strain distribution (e_{xx}) and strain energy by GPA (Figure 5a–i and Supporting Information). Here, the strains from the original curvature of the conjugated planes were excluded in the calculation of strain energy. The strain maps clearly demonstrate that the residual strains and strain energy increased with decreasing curvatures (Figure 5j), where

more carbon–carbon bonds exhibited larger angles (θ) between the axis of carbon–carbon bond and the slicing direction.

In addition to the displacements of conjugated planes, distortions of carbon-carbon bonds were generated after slicing. The mild strains in the strain maps (Figure 5b,e,h) and smooth peaks in the isometric plots (Figure 5d,f,i) were attributed to spontaneous displacements of conjugated planes, which is a plastic yielding process. By contrast, intense strain cores appeared in the strain maps, accompanied by corresponding sharp peaks in the isometric plots, which were attributed to the distortions of carbon-carbon bonds. For local areas with small curvature in MWCNTs, the atomic rearrangements consisted of both displacements of conjugated planes and distortions of carbon-carbon bonds. With increasing curvature, the smooth peaks corresponding to displacements almost disappeared, and sharp peaks corresponding to bond distortions decreased but still existed. Therefore, the strains and strain energy mainly originated from the distortions at higher curvatures.

The GPA strain maps and corresponding isometric plots also aided the understanding of the breaking process and mechanism. The distortions of carbon-carbon bonds generally exhibited compressing-tensile dislocation dipoles in the strain map. This type of structural transformation is similar to the dislocation dipoles formed under tensile stress. Bond movements and rotations created the dislocation cores, with obvious evidence of the plastic breaking process.^{17,18,22} To further understand the breaking process, nitrogen atoms were doped into the MWCNTs during synthesis, followed by slicing under the same conditions (Figure S7-9). With increasing nitrogen contents (equal to increasing lattice defects and dislocations of carbon atoms), more and sharper peaks corresponding to distortions of carbon-carbon bonds were observed. The greater number of dislocation dipoles indicates that the doped atoms were inclined to become strain centers, and the sharper dislocation dipoles imply that the lattice defects tended to generate stress concentrations. Considering the displacements of graphene lattices and the dislocation dipoles, the plastic breaking mechanism dominated the slicing process of both nondoped and doped MWCNTs.

Effective regulation of MWCNT nanostructures is useful for a wide range of promising applications. A variety of MWCNTs with diameters from several to nearly 100 nm and lengths from tens of nanometers to hundreds of micrometers can be well controlled by regulating the growing process and cutting process. Therefore, the sliced MWCNTs can satisfy various applications. As a demonstration, they were used as an anode in a lithium-ion battery. After forming a necessary solidelectrolyte interface on the surface of an electrode,^{28,29} reversible specific capacities reached ~1380 mAh/g at a rate of 0.2 A/g (Figure S10). The specific capacities decreased with the increasing height because ion transport became less effective along longer pathways, and the hollow space was not fully utilized (Figure S11). The specific capacities were ~ 7 times greater than that of pristine MWCNTs (230 mAh/g) at the same rate (Figure S12). The much higher specific capacity resulted from the effective regulation of the nanostructure. The open ends, aligned structures, and low length/diameter ratio of the sliced MWCNTs suggest that they are promising candidates for increasing the storage capacity and transport ability of lithium ions.

CONCLUSION

In this work, MWCNTs with controllable sizes are cut precisely along the radial direction, and the structural evolution is efficiently investigated through a combination of geometry phase analysis and first-principle calculation. The lattice deformation depends on the anisotropy, chirality, curvature, and slicing rate. In particular, understanding plastic breaking mechanism and the atomic transformations with the impacts of strain rate and initial lattices help to actually reveal a plastic breaking mechanism for both nondoped and doped MWCNTs under cutting. This method may be extended as a general strategy for the characterizations of shear deformations in nanomaterials. The resulting sliced carbon nanotubes with controllable sizes and open ends are promising for various applications, for example, as an anode material for lithium-ion batteries.

METHODS

Synthesis of Sliced MWCNT and Nitrogen-Doped MWCNT Arrays. Aligned MWCNT arrays with heights of 0.5–2 mm were grown on a silicon wafer at 750 °C by chemical vapor deposition.¹¹ The MWCNTs typically showed a diameter of ~8 nm. The MWCNT array was then transferred onto another clear silicon wafer and performed the second-step growth also by chemical vapor deposition but at a higher temperature of 1060 °C. The diameters of the MWCNTs were thus increased to 10-125 nm, depending on the growth time of 10-120 min. Ethylene, hydrogen, and argon were used as the feeding gases with flowing rates of 10, 10, and 110 standard cubic centimeters per minute (sccm) respectively. For the nitrogendoped MWCNT, acetonitrile was used as both carbon and nitrogen sources and carried into the chamber by argon at a flow rate of 30 sccm. The resulting MWCNT arrays were embedded into epoxy resin or a frozen butyl alcohol/N,N-dimethylformamide mixture (volume ratio of 1/3) for sectioning by a diamond blade (Leica RM2265, Leica LN22). The embedding medium was much softer than MWCNTs, and it was mainly used to stabilize the MWCNTs. As expected, the embedding materials can be easily removed (Supporting Information), depending on the application requirement.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b04130.

Details of materials preparation, characterization, theoretical simulation, Figures S1–S15 (PDF)

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Notes

The authors declare no competing financial interest.

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