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Unzipping Carbon Nanotubes: A Peeling Method for the Formation of Graphene Nanoribbons**

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Graphene is currently the most promising star in the realm of condensed-matter physics and has the potential of revolutionizing applications in the field of nanoelectronics.[1] It is the mother of all expanded aromatic carbon modifications. Although graphene represents a basic single layer of the well-known carbon allotrope graphite, it was only recently that the first preparation of this atomically thin two-dimensional material was accomplished.[2] The extension of graphene in one direction yields graphene nanoribbons (GNRs), which can be considered as elongated strips.[3–9] They gradually convert from semiconductors to semimetals with increasing width, indicating the impact of the edge states.[10] This together with their defined shape make them very attractive building blocks for the development of new electronic devices such as field-effect transistors. So far GNRs have been prepared starting from graphite, graphene, or graphene oxide using lithographic,[8,9,11] chemical,[12,13] sonochemical,[14] and synthetic methods[15] and one chemical vapor deposition procedure.[16] However, it proved difficult to obtain GNRs with smooth edges and controllable widths in high yields.[17]

Very recently, two groups have independently reported very elegant methods for GNR production, which are based on the longitudinal unzipping of multiwalled carbon nanotubes (MWCNTs).[10,17] These procedures are very appealing, since they are simple and inexpensive, and lead to GNRs with defined shape. Moreover, GNRs may be produced as MWCNTs are readily available.

In their approach Tour and co-workers[10] started from a suspension of MWCNTs in sulfuric acid, which they subjected to oxidative treatment with 500 wt% $KMnO_4$ for 1 h at room temperature and 1 h at 55–70 °C. The resulting GNRs (Figure 1) are highly soluble in water, ethanol, and other polar solvents. As concluded from transmission electron microscopy (TEM) investigations, the carbon nanotubes are sliced either longitudinally (Figure 2) or in a spiral manner affording straight-edged ribbons.

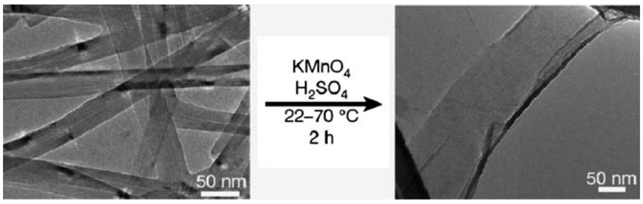

Figure 1. TEM images of MWCNTs (left) and after the transformation into an oxidized graphene nanoribbon (right).[10]

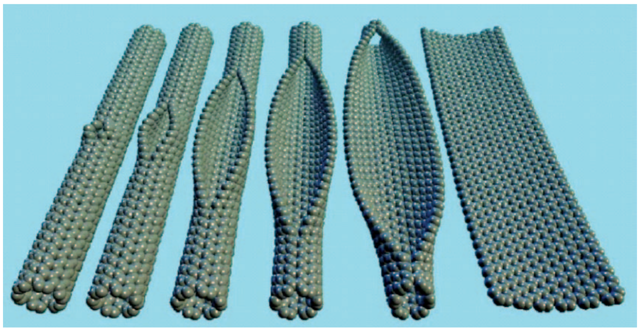

Figure 2. Representation of the sequential unzipping of a carbon nanotube to oxidized graphene.[10]

The authors propose an opening mechanism where in the initial rate-determining step a manganate ester is formed by the addition to an unsaturated bond of the nanotube side wall. The subsequent oxidation is facilitated by the dehydrating medium and leads to an opened diketone defect flanked by β,λ double bonds. Steric repulsion between the two opposing carbonyl groups contributes additional strain energy to the β,λ double bonds making them more prone to the next attack by permanganate. Further opening of the β,λ bonds reduces the steric repulsion between initially formed carbonyl groups. However, at the same time the continued unzipping increases the bond angle strain by enlarging the hole, making the β,λ double bonds more and more reactive (Figure 2). The strain in the system is relieved only when the outermost nanotube has been completely opened to give the GNR sheet. The

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ketones terminating the GNR sheets can be further oxidized to the carboxylic acids. This mechanism nicely explains the preference of the sequential over random opening. Similar peeling processes have been observed for single-walled carbon nanotubes (SWNTs); however, their subsequent disentanglement was reported to be more difficult.[10]

Atomic force microscopy (AFM) revealed the presence of single-layered GNRs, which can be easily dispersed and display uniform widths and predominantly straight edges over their entire length. The rate of unzipping was found to be independent of the diameter of the nanotubes. The GNRs were further characterized by scanning electron microscopy (SEM), infrared spectroscopy, thermogravimetric analysis (in order to investigate the nature of the oxygen functionalities), and X-ray diffraction analysis. Oxygen functionalities located at the edges and the surface can be removed to a certain extent by reductive treatment with hydrazine in order to restore some of the lost conjugation induced by the sp^3 defects. This leads at the same time to a significant increase in the electrical conductivity. However, the corresponding GNRs still contain residual oxidized defect sites, and their electronic characteristics are inferior to those of mechanically exfoliated graphene sheets.

The group led by Jiao, Zhang, and Dai[17] followed a similar unzipping approach to prepare GNRs. They partly embedded MWCNTs in a poly(methyl methacrylate) (PMMA) layer, which served as an etching mask (Figure 3 a,b). This procedure guaranteed that a narrow strip of the MWCNTs is not covered by the PMMA. Unzipping was then accomplished by exposure of the PMMA–MWCNT film to a 10 W Ar plasma for various times (Figure 3 d–g). Preferably strip of the MWCNT not covered by the mask was etched by the plasma. Depending on the etching time, the diameter, and number of layers of the starting MWCNTs, single-, bi- and multilayer GNRs and GNRs with inner CNT cores were formed. Finally, the PMMA film was contact printed on a silicon substrate, and the polymer film was removed by treatment with acetone vapor (Figure 3 h)

AFM investigations revealed that unlike for previous GNRs the edges of the obtained ribbons are very smooth. Moreover, the GNRs are uniform in width and length, because the quasi-one-dimensional CNT templates have uniform diameters along their lengths. The widths of the GNRs are mostly in the range between 10 and 20 nm, corresponding to half of the circumference of the starting MWCNTs which have a mean diameter of roughly 8 nm. As a consequence, the width distribution of the resulting GNRs is much narrower than that of other GNRs.

The GNRs were characterized further by Raman spectroscopy, which in general serves as a very powerful tool for the investigation of carbon-based materials. In particular the line shape of the second-order Raman band (2D) is very sensitive with respect to the number of deposited layers; in this case the presence of single-, bi-, and trilayer GNRs was suggested. Furthermore, the intensity ratio of the D and G bands (I_D/I_G) revealed the presence of very defect-poor sheets. The defects are mainly due to the open edges. More defects were obtained when the etching time was increased to 20 s or longer.

The authors were also able to engineer field-effect transistor devices with the GNRs serving as layers. It was demonstrated that the GNRs exhibit quantum-confined semiconducting characteristics in contrast to bulk graphene, with much weaker gate modulation conductance. For the narrowest ribbons with a width of ≈ 6 nm, I_{off}/I_{on} ratios of >100 were measured. As a result of the presence of physisorbed O_2, p-doping behavior was observed. The resistivity of the devices at the Dirac point for 10–20 nm wide GNRs was 10–40 kΩ, similar to the resistivity of lithographically prepared GNRs. The charge carrier mobilities of the GNRs are very high and only about 10 times lower (caused by edge scattering) than those of large two-dimensional graphene sheets, which have the highest mobilities of any material known to date.

Although the GNRs obtained by these new unzipping methods have electronic characteristics inferior to those of wide, mechanically peeled sheets of graphene,[10] they open the door for the large-scale production of ribbons with controlled structure and quality[17] and as a consequence with tunable properties. In particular, if GNRs can be prepared as highly ordered sub-10 nm strips, they have potential for room-temperature transistor applications. This represents an im-

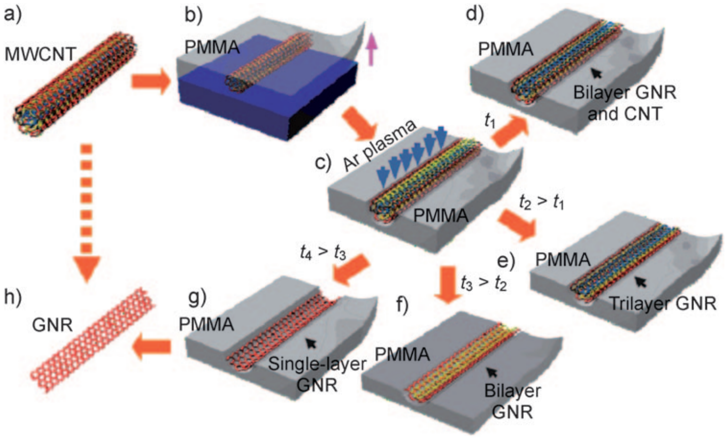

Figure 3. GNR formation: MWCNTs are embedded in PMMA and then treated with an Ar plasma.[17]

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portant step for the replacement of the classical silicon-based devices and further heralds the carbon age of modern computer design and nanotechnology.

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