

Sharpening the Chemical Scissors to Unzip Carbon Nanotubes: Crystalline Graphene Nanoribbons

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Carbon is one of the most abundant elements in nature. It is essential to living organisms and it constitutes building blocks of a wide variety of compounds. It is the framework of complex molecules such as fats, steroids, hydrocarbons, oil, soot, solvents, and many others. Carbon possesses four electrons in its outer valence shell, and it can also form natural crystalline forms such as diamond and graphite. However, over the last 20 years, novel nanoscale carbon crystalline forms have been predicted and synthesized: fullerenes (cage-like molecules), graphene (individual sp^2 hybridized carbon sheets), carbon nanotubes (rolled graphene sheets), graphene nanoribbons, and diamond clusters (sp^3 hybridized carbon nanoparticles), among others.

This Perspective article is intended to summarize important aspects related to the morphology, synthesis, and physicochemical properties of different types of carbon systems: from flat microscale carbon particles to flat nanoscale carbon systems, passing through the round cage-like molecules. However, this account intends to provide the reader with useful information related to the importance of defects in sp^2 -like hybridized carbon layers and the new type of chemistry that arises from nanoscale carbon particles and cage-like molecules. Special attention is centered in the unzipping of carbon nanotubes so as to form graphene nanoribbons. The new results obtained by the Tour group will be highlighted,¹ as well as the challenges in the chemistry, physics, and engineering of defects in carbon nanostructures, and their possible applications.

The Round Nanocarbon World (From 1985 Onward). Nanocarbon research started after the discovery of C_{60} (buckminsterfullerene) in the mid-1980s.² Five years later, these

beautiful cage molecules were synthesized in bulk using an arc discharge between graphite electrodes.³ The successful isolation of these structures⁴ permitted the development of fullerene chemistry,^{5–7} which was different from conventional organic chemistry due to the curvature of the hexagons induced by the presence of pentagons.

In the early 1990s, the theoretical concept of curvature in graphitic structures became more important because, in addition to pentagons, heptagons and octagons could also be introduced into hexagonal sp^2 hybridized carbon networks.⁸ For example, because of the presence of pentagons,^{9,10} it was possible to explain the sphericity of carbon black nanostructures observed experimentally.¹¹ Therefore, the nanocarbon world started to curve, and the concept that graphite could only be flat started to change among scientists. A few months later, Sumio Iijima reported the first electron diffraction patterns of “graphitic microtubules”, now termed nanotubes,¹² which were produced *via* arc discharge (the same process used for obtaining fullerenes). These electron diffraction patterns revealed that graphene sheets could be rolled over so as to form perfect and concentric graphite tubes. In addition, this report showed that the tips of the tubes contained pentagons in order to achieve closure, the same as fullerenes.¹³ It is worth mentioning that Endo, Koyama, and Oberlin also reported the structure and discussed the growth mechanism of perfect graphite tubes *via* chemical vapor deposition (CVD) in 1976.¹⁴

Soon after Iijima’s publication in 1991, a tremendous amount of theoretical and experimental research was devoted to carbon nanotubes and nanofibers, and the number

ABSTRACT It has recently been demonstrated that graphene nanoribbons can be mass-produced by unzipping carbon nanotubes. At present, wet chemical routes *via* acid oxidation appear to be the most effective and scalable. Although it was believed that this route resulted in highly defective nanoribbons with low electrical transport properties, a research group led by James Tour at Rice University has now realized that it is indeed possible to obtain highly crystalline graphene nanoribbons exhibiting high electrical conductivities, which could be used in the fabrication of field effect transistors and other devices. The results indicate that a defect-engineering approach could be used to control the straightness and length of the ribbons using oxidation reactions at relatively high temperatures (*e.g.*, 60 °C). It has been shown that defects are critical in tailoring the physicochemical properties of graphene-like nanomaterials such as nanoribbons. However, this is the tip of the iceberg, and more edge chemistry and physics is still needed to develop and to produce real graphene nanoribbon devices for use in the market.

See the accompanying Article by Higginbotham *et al.* on p 2059.

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of publications increased almost exponentially each year (Figure 1a). Subsequently, it was demonstrated that the CVD method reported by Endo¹⁵ was the most controllable one to produce large quantities of different types of carbon nanotubes: single-walled, double-walled, and multiwalled.

The theory of single-walled carbon nanotubes (SWNTs) developed rapidly, and it was predicted theoretically that the tubules could exhibit either semiconducting or metallic^{16–18} behavior depending on the chirality (that is, the way the hexagons are aligned along the tube axis). Armchair tubes were predicted to be all metallic, and zigzag tubes could be semiconducting as well as metallic. These predictions were confirmed 7 years later by Dekker's group in The Netherlands¹⁹ and Lieber's group in the US.²⁰

The Flat Graphene Nanoworld (from 2004 Onward). The fact that different chiralities within a nanotube result in different electronic behavior stimulated theoretical calculations of flat sp^2 carbon hybridized strips, now termed graphene nanoribbons (GNRs). The first electronic calculations of GNRs were performed by Nakada, Fujita, Dresselhaus, and Dresselhaus in 1996.²¹ In particular, graphene ribbons have been predicted to be metallic if their edges exhibit a zigzag morphology, whereas armchair edges can give rise to either semiconducting or metallic transport.²¹ More interestingly, it has been predicted and confirmed experimentally that GNRs less than 10 nm wide behave as semiconductors, independent of their edge patterns. Narrow GNRs are thus excellent candidates for use in electronic devices, such as field effect transistors, which form the basis of microchips in computers.

Although research into the ribbon edge structure was very exciting, during the last decade of the 20th century, experimental researchers were more attracted to the curved nanoworld of nanotubes

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and fullerenes. It was not until 2004 and 2005 that graphene caught on, when Novoselov, Geim, and co-workers reported a synthesis method based on the peeling of graphene sheets and their electronic properties.^{22,23} Therefore, these reports initiated a new "flat" era in carbon nanoscience, and since then, the number of publications related to graphene (2D systems) and nanoribbons (1D systems) has increased; it is expected that they will continue to grow rapidly in the coming years (Figure 1b).

At present, researchers around the world are directing their studies toward the bulk synthesis of individual graphene sheets and nanoribbons in order to characterize their physicochemical properties. Until 2009, most of the techniques to produce these flat nanoscale systems involved the peeling of highly oriented pyrolytic graphite (HOPG). Over the last year, the bulk CVD synthesis of graphitic nanoribbons²⁴ and the unzipping of multiwalled carbon nanotubes (MWNTs) to form GNRs were reported.^{25–30}

New Graphene Synthesis: Unzipping Carbon Nanotubes. To date, it is possible to classify unzipping nanotube processes as follows (Figure 2): (a) wet chemical methods, involving acid reactions that start to break carbon–carbon bonds (*e.g.*, H_2SO_4 and $KMnO_4$ as oxidizing agents);²⁶

(b) physicochemical methods, by embedding the carbon nanotubes in a polymer matrix followed by Ar plasma treatment;²⁷ (c) intercalation-exfoliation of MWNTs, which deals with the removal of the tube caps using acid treatments, followed by treatments in liquid NH_3 and Li, and the subsequent exfoliation-heat treatment;²⁸ (d) catalytic approach in which metal nanoparticles cut the nanotube longitudinally like a pair of scissors;²⁹ and (e) the electrical method, by passing an electric current through a nanotube.³⁰

The idea of longitudinal cutting of MWNTs to form GNRs appears to be extremely powerful in terms of mass production. This is mainly because several companies around the world, including Mitsui, Showadenko, Bayer, Nanocyl, Swan Ltd., and others in China and elsewhere, are able to generate tons of carbon nanotubes per year using the CVD process. Therefore, by unzipping MWNTs into nanoribbons, the nanoribbons could also be mass produced. However, efficient and low-cost unzipping processes still need to be developed and scaled efficiently.

Defects in Graphene: The Chemistry and Physics Start. Defects are always present within graphite-like systems such as single- and multiwalled carbon nanotubes. The amount and type of defects depend on the production method, including the processing temperatures. For example, arc discharge and laser ablation methods involve extremely high temperatures, 2500–3500 °C,³¹ and these processes result in the generation of highly crystalline nanotubes. On the other hand, CVD techniques usually involve lower temperatures ranging from 650–1200 °C.³¹ These tubes contain a large number of defects and the walls can possess vacancies, carboxyl groups, or other elemental dopants. In this context, Tour's group has observed that unzipping of arc-discharged MWNTs occurs less often; this is because defects

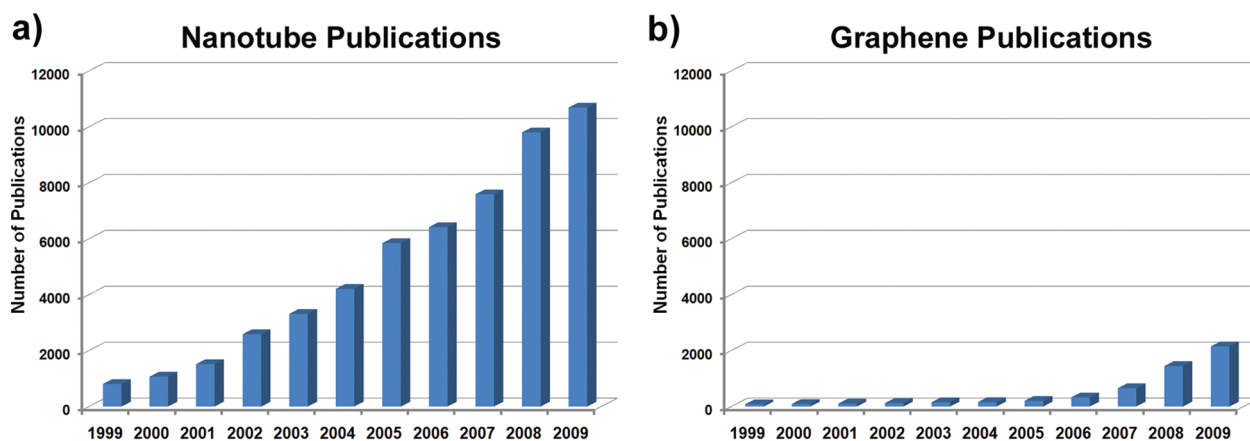


Figure 1. Number of publications extracted from the Web of Science over the last 10 years (1999–2009), showing how the (a) nanotube and (b) graphene fields have developed. It is important to note that the number of “graphene” publications in 2009 is equivalent to the number of “nanotube” publications published in 2002, and it is expected that graphene papers will increase rapidly in the coming years. The results were obtained using a keyword search for “nanotube” and “graphene”.

are not very common in these highly crystalline nanotubes.²⁶

In practice, it is difficult to identify the type of defects contained in graphite-like systems, and researchers have not been able to distinguish them systematically. However, depending on the nature of the defective surface, the chemical activity of these systems may be quite different.

For example, it is still complicated to estimate the concentration of defects in as-prepared nanotubes and to evaluate the effects of purification and separation treatments. It has been reported from direct chemical titration that SWNTs

produced by pulsed laser ablation contain more than 4% defective sites after purification of the samples by acidic oxidation.³² Arguments exist in the literature that these defects could be pentagon–heptagon pairs, possibly grouped in Stone–Thrower–Wales type defects (see below), which would provide carbon–carbon double bonds where chemistry and functionalization can take place.³³

In general, defects within sp^2 hybridized carbon systems can be categorized in five different groups (Figure 3):

(1) *Structural defects*, related to imperfections that significantly distort the curvature of the hexagonal carbon honeycomb structure. These defects are usually caused by the presence of nonhexagonal rings (e.g., pentagons, heptagons, or octagons (Figure 3a)).

(2) *Topological defects*, occurring on the nanotube surface, which do not result in large curvature distortions (Figure 3b). In particular, these defects could be 5–7–7–5 pairs embedded in the hexagonal network or Stone–Thrower–Wales (STW-type) defects^{35,36} that could be created by rotating a

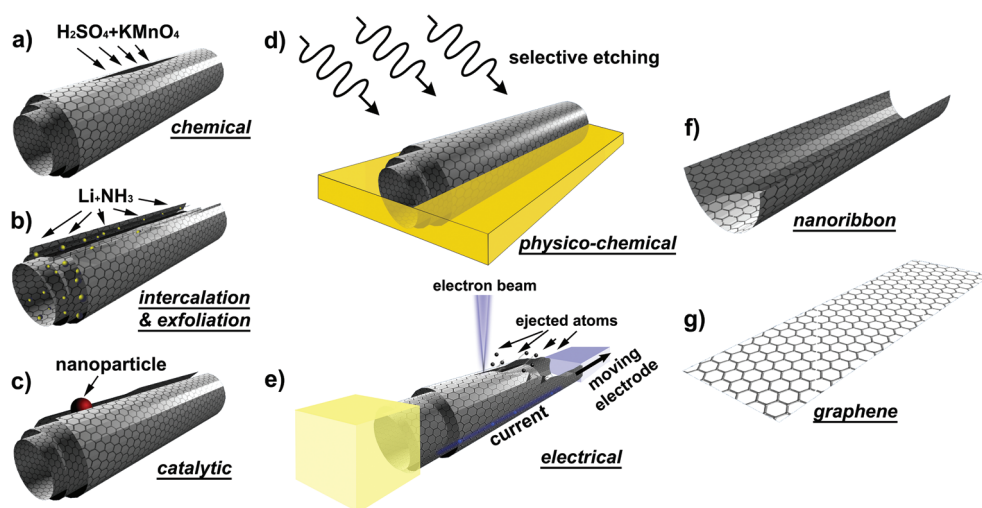


Figure 2. Sketch showing the different ways nanotubes could be unzipped to yield graphene nanoribbons (GNRs): (a) chemical route, involving acid reactions that start to break carbon–carbon bonds (e.g., H_2SO_4 and $KMnO_4$ as oxidizing agents);²⁶ (b) intercalation-exfoliation of MWNTs, involving treatments in liquid NH_3 and Li, and subsequent exfoliation using HCl and heat treatments;²⁸ (c) catalytic approach, in which metal nanoparticles “cut” the nanotube longitudinally like a pair of scissors;²⁹ (d) physicochemical method, by embedding the tubes in a polymer matrix followed by Ar plasma treatment;²⁷ and (e) the electrical method, by passing an electric current through a nanotube. The resulting structures are either (f) GNRs or (g) graphene sheets. Image courtesy of A.R. Botello-Méndez.

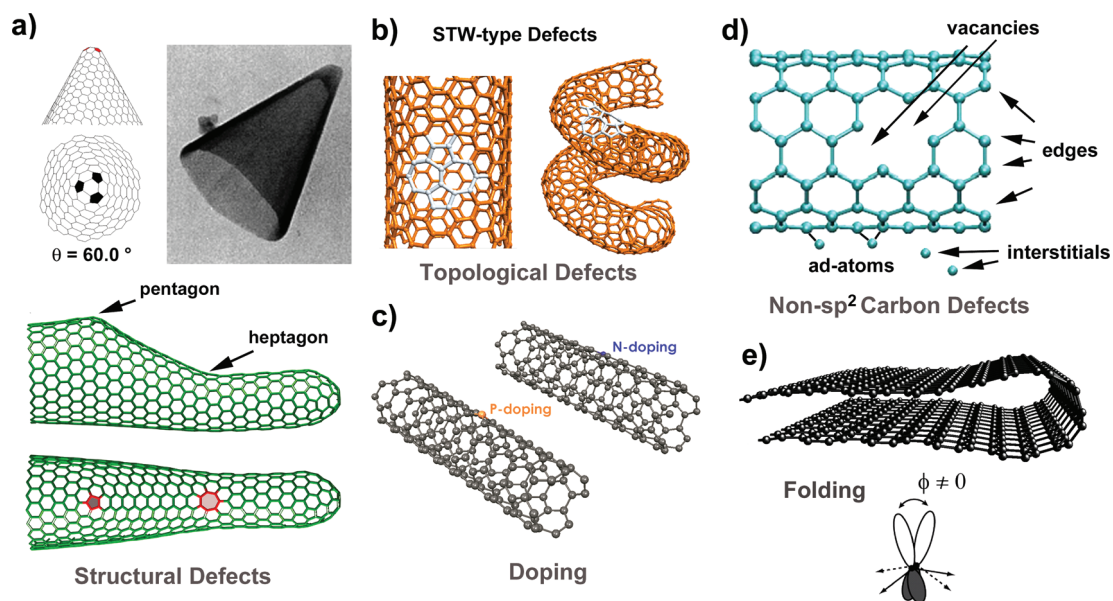


Figure 3. Schematic models representing different types of defects in graphene-like materials. (a) Structural defects induce significant structural changes caused by the presence of pentagons or heptagons within the hexagonal sp^2 -hybridized carbon lattice. Image courtesy of M. Endo and T.W. Ebbesen. (b) Topological defects, also termed Stone–Thrower–Wales defects, do not result in big structural changes. Shown here is the formation of 5–7–7–5 pairs created by rotating an individual carbon–carbon bond 90° . Image courtesy of H. Terrones. (c) Doping consists of replacing a carbon atom with another element within the hexagonal lattice (here, N and P). Adapted from ref 34. Copyright 2010 American Chemical Society. (d) Non- sp^2 -hybridized carbon defects, including vacancies, edges, adatoms, interstitials, carbon chains, etc. (e) Folding-induced defects, which result from significant deformation of the graphene sheet, thus altering the π orbitals. The direction of the π orbital is then called the π orbital axis vector (POAV). The angle $\theta_{\sigma\pi}$ between the POAV and a σ direction (i.e., a bond) indicates the degree of “pyramidalization” and the hybridization. For $\theta_{\sigma\pi} = 90^\circ$ (planar system), the σ orbitals are in a sp^2 hybridization and the π orbital is a pure p_z orbital. For a folded graphene sheet, $\theta_{\sigma\pi}$ has an intermediate value which decreases as the inverse of the radius of the curvature of the folding, and reaches 90° at the limit $R \rightarrow \infty$. Image courtesy of A.R. Botello-Méndez.

carbon–carbon bond 90° within four neighboring hexagons, thus resulting in the transformation of two pentagons and two heptagons.^{10,37}

(3) *Doping-induced defects*, arising from substitutional noncarbon atoms embedded in the hexagonal lattice (Figure 3c).

(4) *Non- sp^2 -carbon defects* (e.g., adatoms, edge sites, vacancies, etc.) caused by the presence of highly reactive carbons such as dangling bonds, carbon chains, interstitials (free atoms trapped between SWNTs or between graphene sheets), edges (open nanotubes), adatoms, and vacancies (Figure 3d).

(5) *High-strain folding of graphene sheets* (loop formation), which can be induced by annealing two adjacent graphene layers (Figure 3e).

In fullerene (or carbon cage) chemistry, the main type of defect is *structural*, which deals with the presence of pentagonal rings that

induce a highly curved and reactive molecule caused by the mixture of π and σ orbitals. In nanotube chemistry these structural defects mainly occur on the caps (where penta-

gons are located). Narrow or highly curved nanotubes (usually <1 nm diameter) would also be reactive. In highly crystalline SWNT samples, the caps are a small portion of the structure and other highly curved areas are not present since the nanotubes possess diameters larger than 1 nm. Therefore, graphene and nanotube chemistry require a better understanding of the defects mentioned above, in order to induce and control strong (or weaker) covalent (or π – π) interactions with other molecules, atoms, or clusters.

Sharpening the Chemical Scissors for Unzipping Nanotubes. Defects are generally present in high or low concentrations in most of the graphite-like materials produced. These defects become the reactive sites and lead to the chemistry and physics of graphitic materials. However, a great majority of the published work in the field does not emphasize the importance of defects, and most of the literature assumes that

Graphene and nanotube chemistry require a better understanding of defects, in order to induce the formation of GNRs and to control their interactions with other molecules, atoms, or clusters.

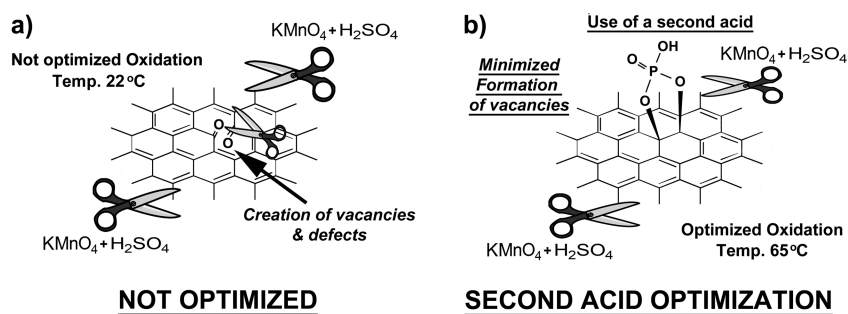


Figure 4. Sketches representing the nonoptimized and the optimized oxidation processes used to unzip carbon nanotubes. (a) Besides unzipping the tubes, the use of KMnO_4 and H_2SO_4 are also responsible for creating a large number of vacancies or “holes” in the graphene structure; these holes modify significantly the electronic and mechanical properties of the graphene nanoribbons. (b) The use of KMnO_4 and H_2SO_4 in conjunction with a second acid such as H_3PO_4 at 65 °C. In this case, the tubes are mainly cut along their length and the formation of vacancies is minimized due to the protection of the diol groups by the second acid. Adapted from ref 1. Copyright 2010 American Chemical Society.

pristine tubes or graphene are defect-free or very close to that. Therefore, chemists and physicists should start considering graphene defects in order to start developing nanotube and graphene chemistry further.

In this context, the chemical method developed at Rice University by Tour and co-workers²⁶ has now been improved further to yield highly crystalline carbon nanoribbons, as reported in this *ACS Nano* issue.¹ In this work, the Tour group has demonstrated that the nanotube oxidation process used to unzip MWNTs can be controlled. In particular, these authors have shown that it is possible to significantly inhibit the formation of “holes” within the unzipped sheets (defective sites in which vacancies are dominant), since a large number of additional defects could significantly alter the electronic and mechanical properties of the resulting GNRs (Figure 3).

It is therefore clear that better control and understanding of the various defects in graphene ribbons should be addressed from experimental and theoretical standpoints. If the reactivity and behavior of different defects are known, their abundance could be determined, and the electronic, magnetic, chemical, thermal, and mechanical properties of graphene-based nanostructures could be controlled in principle.

In this issue of *ACS Nano*, Higginbotham *et al.*¹ have demonstrated that it is possible to optimize the nanotube unzipping process using a clever chemical oxidation process, and to maximize the yield of the resulting GNRs. In particular, Tour and co-workers observed that chemical oxidation is more efficient at relatively high temperatures (60 °C) and that a second acid ($\text{C}_2\text{HF}_3\text{O}_2$ or H_3PO_4) should be added to the $\text{H}_2\text{SO}_4/\text{KMnO}_4$ mixture for optimal yield (Figure 4). The presence of the second acid (*e.g.*, H_3PO_4) inhibits the creation of vacancies in the GNRs due to the protection of the diol groups. Interestingly, the degree of oxidation could be adjusted by controlling the amount of the oxidizing agent (KMnO_4) in the reaction.

Tour and co-workers observed that chemical oxidation is more efficient at relatively high temperatures for the unzipping process and that a second acid should be added for optimal yield.

For example, when 10% of a second acid (TFA or H_3PO_4) was added to the reaction mixture of $\text{H}_2\text{SO}_4/\text{KMnO}_4$, it was possible to control the oxidation of the nanoribbon edges with hydroxyl groups, and fewer oxygen compounds such as $\text{C}=\text{O}$ and COOH functionalities were reduced (Figure 4). These results are important in nanoribbon chemistry, and X-ray photoelectron spectroscopy (XPS) is a key tool to monitor different functional groups. Consequently, it has been demonstrated that defect-based control of the reactivity of the ribbons with hydroxyl groups is possible and further unexplored graphene ribbon chemical reactions still need to be tested.

From an electronic materials point of view, the presence of these hydroxyl groups affects the nanoribbon transport, and they should be removed in order to enhance the conductivity of the ribbons. In this context, Tour’s group demonstrated that hydrazine was very efficient in removing oxygen from the graphene nanoribbons, thus improving the electrical conductivity. The Rice group noted that the conductivity of the ribbons after oxygen removal corresponded to *ca.* 35 S/cm.

It is also noteworthy that the optimized process reported in this issue using a second acid at elevated temperatures, yielded much longer (>5 μm) and narrower ribbons (<100 nm), and exhibited sharper

and more linear edges (*i.e.*, more atomically perfect), when compared to previous reports in the literature (Figure 5). This indicates that the nanoribbons were highly crystalline, and these results will stimulate further experiments regarding the fabrication of polymer composites, biosensors and chemical sensors, and even electronic devices such as field effect transistors.

The mechanism for opening MWNTs was explained in terms of the oxidation of alkenes by permanganate in acid, which has been recently confirmed using theoretical calculations.³⁸ The kinetics of unzipping resemble that of chain-reaction polymerization: propagation must occur much faster than initiation, and the presence of defects in the initial pristine MWNTs appears to be important because the same process used with arc-discharge nanotubes instead of CVD MWNTs results in a less efficient unzipping process.²⁶ The authors explained that in the optimized process, the second acid improves the chemoselectivity by minimizing (or controlling) the oxidation process.

The novel GNRs display a higher degree of edge oxidation with diol groups but lower levels of "hole" formation, usually represented by carbonyl and carboxyl molecules. The electrical measurements of ribbon devices indeed revealed that the conductivities of hydrazine-reduced GNRs reported by Higginbotham *et al.*¹ were 2–20 times higher than the nonoptimized graphene nanoribbon reactions reported earlier.

Future Work and Applications. The production of GNRs by unwrapping carbon nanotubes appears to be a viable large-scale route. Although wet chemical routes appear to be scalable for mass production of nanoribbons, other physical and chemical techniques should be implemented and explored. It is clear that GNRs could be dispersed in suspensions owing to the reactivity of the large number of edges

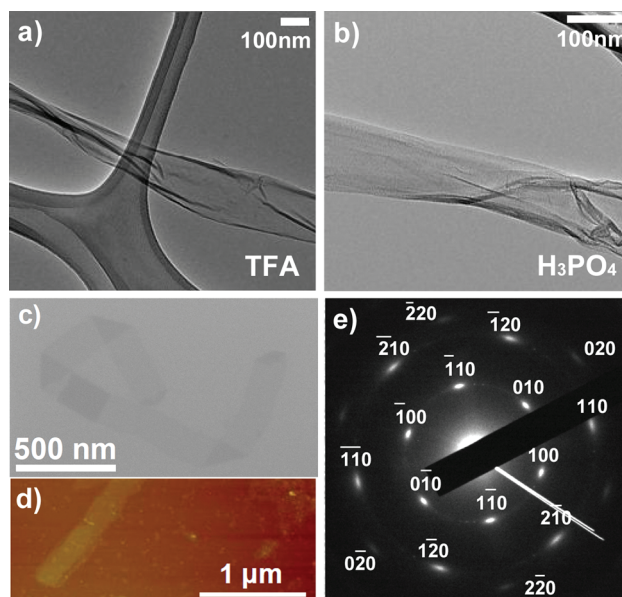


Figure 5. (a,b) Transmission electron microscopy (TEM) images of graphene nanoribbons obtained by unzipping CVD-grown multiwalled carbon nanotubes, using the optimized method involving a second acid (TFA or H_3PO_4) in the presence of KMnO_4 and H_2SO_4 at 65°C ; (c) TEM image of a graphene nanoribbon showing various bends produced using the method by Higginbotham *et al.*; (d) atomic force microscopy (AFM) image of a graphene nanoribbon segment produced by the optimized oxidation method using a second acid (H_3PO_4) at 65°C , in addition to KMnO_4 and H_2SO_4 , and (e) electron diffraction pattern of a few-layer graphitic nanoribbon obtained using the same conditions as those shown in panel d. Note the bright spots corresponding to the hexagonal lattice. The pattern is indexed for visualization purposes. (All images showed in this figure are courtesy of J. M. Tour, Rice University). Panels c and d are adapted from ref 1. Copyright 2010 American Chemical Society.

sites. Therefore, edge chemistry and physics of the ribbons, a field which is just beginning, should now

lead to novel catalytic reactions, sensor fabrication, the production of field effect transistors, the generation of electrodes for Li-ion batteries, the assembly of heavy metal filters, the fabrication of highly conducting and transparent polymer composites and other composites with metals and ceramics, and more.

However, it is also important to understand the chemistry and physics of the different types of defects in graphene-like nanostructures (Figure 3). Defect-controlled engineering is needed in order to tailor the chemical, electronic, mechanical, magnetic, and thermal properties of these nanoflat carbon structures known as graphitic nanoribbons.

Finally, it is foreseen that novel methods still need to be developed and improved to produce doped GNRs. It is clear that GNRs produced by unzipping carbon nanotubes, now produced in quantities of tons

The electrical measurements revealed that the conductivities of hydrazine-reduced graphene nanoribbons reported by Higginbotham *et al.* were 2–20 times higher than the nonoptimized reactions reported earlier.

per year, could be used for making novel electronic devices, conducting paints, robust polymer composites, drug delivery agents, and many others.

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