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High Temperature Structural Transformations of Few Layer Graphene Nanoribbons Obtained By Unzipping Carbon Nanotubes

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High temperature structural transformations of few layer graphene nanoribbons obtained by unzipping carbon nanotubes†

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Multilayer and few layer graphene nanoribbons produced by oxidative unzipping of carbon multiwalled carbon nanotubes (MWNT $10 > N > 5$) and $N \leq 4$ carbon few walled nanotubes (FWNT) were annealed at temperatures up to 1400 °C and the resulting carbon nanostructures were studied. Transmission electron microscopy imaging of the graphene nanoribbons annealed in bulk shows higher structural stability in larger width multilayer graphene nanoribbons than in narrow few layer nanoribbons. Fringes of dark and bright contrast along the edges of MLG indicate edge closure within the layers of the stacked graphene nanoribbons. On the other hand, narrow FLG nanoribbons fuse within each other or collapse when annealed leading to three different nanostructures: large area MLG plates several microns wide, graphitic onions of approximately 100 nm in diameter and nanocrystalline/amorphous composite particles.

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Introduction

Since the first preparation of single layer graphene by mechanical exfoliation using the scotch tape method,¹ many studies have shown the unique mechanical,² electronic,³ electrochemical⁴ and catalytic properties⁵ of individual graphene sheets. The electrical properties are extremely dependent both on the dimensions of the graphene layer⁶ as well as on the presence of attached functional groups.⁷ Among the different methods for the production of graphene, and derivative methods for producing graphene nanoribbons, mechanically exfoliated graphene has the highest electronic conductivity due to the low defect content.⁸ However its use is not suitable for mass scale production because of very low yields and consequent high cost. Graphene produced by chemical vapour deposition (CVD) on top of metallic substrates is becoming more important for applications in which large films are required, although single crystal films have not yet been produced.⁹ Chemically converted graphene produced by

oxidation of graphite and further chemical and/or thermal reduction produces bulk material quantities having higher defect concentrations,¹⁰ broad dispersion in graphene shape and size, and associated decrease of such properties as electronic conductivity.

Narrow graphene ribbons with widths of 10 nm or less have additional interest, since they are semiconducting, with bandgaps dependent on the width of the ribbon.⁶ A simple, scalable method has been described for the preparation of bulk quantities of high aspect ratio graphene nanoribbons by chemical unzipping of MWNTs.¹¹ Interestingly, depending on the aspect ratios of the initial MWNTs and their diameters, number of walls, and defect content, the final properties of the graphene oxide or graphene nanoribbons can be, in theory, tailored.¹¹ However, depending upon reaction conditions, chemical unzipping can result in various degrees of structural degradation. Initial studies on the production of unzipped graphene nanoribbons used MWNTs made by chemical vapor deposition (CVD), which had outer diameters of 60–100 nm and an average of 20 walls.¹¹ Smaller diameter nanotubes with fewer walls are suitable for practical applications in electronics.⁶

The narrow graphene nanoribbons produced by oxidative unzipping are typically annealed prior to their use in devices^{12,13} or electrodes.^{14,15} While there are studies dealing with the evolution of functional groups on the reduced graphene nanoribbons showing them to be stable when annealed up to 800 °C,¹⁶ the morphological changes that the graphene nanoribbons undergo when annealed at higher temperatures are unknown, and it is the purpose of the present work to study these structural changes.

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† Electronic supplementary information (ESI) available: PXRD and Raman of FWNTs before and after unzipping, Raman spectra of MLG and FLG after annealing, comparative TEM of edges of MWNTs, unzipped MLG nanoribbons and annealed MLG nanoribbons, TEM image of a bundle of FWNTs and TEM images of the products after annealing FLG nanoribbons at 1050 °C. See DOI: 10.1039/c3ta13292g

High resolution imaging of carbon nanotubes and graphene in the transmission electron microscope has been challenging due to the low kick-off voltage damage threshold of these carbonaceous materials, which is above 60 kV.¹⁷ Decreasing the voltage at least to 80 kV is one route towards imaging the carbonaceous nanostructures without causing excessive damage and/or modification. Combined with the low voltage, aberration correctors are used in the electron microscopes to achieve atomic resolution.¹⁸ On the other hand, highly crystalline graphene ribbons show a higher resistance to the electron beam and high quality imaging can be performed even at 200 kV.¹⁹ Highly crystalline material is achieved, for example, through high temperature annealing that can simultaneously reduce the graphene oxide to graphene.²⁰ Transmission electron microscopy (TEM) studies on annealed graphite and graphite oxide have shown that edge reconstruction to nano-tube-like surface structure can occur, and modeling suggests that such edge reconstruction can occur in nanosecond time periods at high temperatures.²¹ In the case of multilayer graphene, edge closure by joining together reactive open edges of two adjacent layers during high temperature annealing has been shown to give rise to straight edges, which in high resolution TEM (HRTEM) appear as lines of dark and light contrast with a 3.5 Å spacing.²²

It is the aim of this work to use TEM and HRTEM to study the structural evolution during thermal annealing for narrow graphene ribbons produced by unzipping MWNT and carbon few-wall nanotubes (FWNTs). Unlike the carbon nanotubes that are traditionally used for chemical transformations, these precursor nanotubes were never subjected to the degradative effects of ultrasonic dispersion. Also, a 200 kV transmission electron microscope was deployed for structural studies since high temperature annealings should render materials with high resistance to the electron beam. The effects of nanotube width and number of stacked graphene nanoribbons on longitudinal edge reconstruction will be characterized, which is important for determining the properties of the graphene nanoribbons.

Experimental

Vertically aligned MWNT forests were grown by CVD using acetylene gas as the carbon source and a silicon wafer substrate, which was coated with a 1–3 nm thick layer of Fe catalyst by e-beam deposition.^{23,24} The substrate was loaded into a quartz tube furnace pre-heated to 700 °C in a mixture of 750 sccm Ar and 100 sccm H₂. After 5 minutes of residence time at furnace temperature, the MWNT forests were grown in 2 to 5 minutes by adding 50 sccm of C₂H₂ to the gas mixture. Using ethylene gas as the carbon precursor for CVD, FWNTs forests were produced over a period of 2 hours at 760 °C in an argon-10% hydrogen atmosphere. Silicon wafers coated with 10 nm of Al₂O₃ and 1.5 nm Fe were used as substrates.

Nanotube unzipping was accomplished by applying the method of Kosynkin *et al.*¹¹ In brief, 30 mg of MWNTs or FWNTs were stirred in 30 ml of H₂SO₄ for 1 hour and then 500–850 wt% of KMnO₄ was added, where the precise amount of added KMnO₄ and the oxidation time was optimized for each type of

carbon nanotube. After oxidative unzipping and washing of the produced graphene nanoribbons with H₂O₂, HCl (35%) and a methanol-ether (1 : 1) mixture deeper cleaning process was carried out. This involved a three-times-repeated process of mild bath sonication for 30 minutes, centrifugation at 15 000 rpm, discard of the supernatant, and redispersion of the precipitate. Finally, dialysis for one week in deionized water was performed inside SnakeSkin dialysis tubing (10 K MWCO, Pierce), changing the water every 12 hours.

In order to follow nanotube-to-nanoribbon conversion for bulk samples, X-ray diffraction (XRD) data was collected in the 2θ range between 3° and 40° using a Rigaku-Ultima III diffractometer that deployed CuK α radiation. As a first step, paper-like sheets used for this analysis were prepared on top of a polytetrafluoroethylene filtration membrane by filtration of liquid-dispersed graphene oxide nanoribbons, drying the sheets, and then peeling the sheets from the filtration membrane. These sheets were subsequently subjected to high temperature thermal annealing in inert or reducing atmospheres, with the goal of reducing the graphene oxide nanoribbons. Annealings were performed at 1050 °C for 2 hours under argon flow or at 1300–1450 °C for 1 hour in vacuum in a graphite furnace.

Raman spectra were collected on a Jobin Yvon HORIBA spectrometer, type Labram HR, using 633 nm laser wavelength. Raman spectra were collected on samples prepared by drop casting of unzipped graphene oxide nanoribbons dispersions in isopropanol on top of silicon wafer substrates.

TEM and HRTEM were performed in a JEOL 2100-FEG electron microscope at an accelerating voltage of 200 kV. Fragments of sheets composed of multilayer or single layer graphene and graphene oxide nanoribbons were dispersed in isopropanol and bath sonicated for 30 minutes. A drop of the suspension was evaporated on a copper grid covered with lacey carbon. Finally, the solvent was completely evaporated by thermal treatment of the TEM grid at 150 °C in argon flow for 1 hour to avoid the formation of amorphous material under the electron beam.

Results and discussion

XRD and Raman

Macroscopic aspects of the unzipping process are usefully followed by powder X-ray diffraction. This analysis method enables optimization of the reaction time and KMnO₄ concentration used for nanotubes having differing lengths, diameters, number of walls, and defect concentrations. It has also been shown that differences in the oxidizing medium lead to different quality material.²⁵ In the case of MWNT grown as vertically aligned forest by CVD,²³ starting tubes with diameters of 5–15 nm, 6–12 walls, and lengths of approximately 0.5 μ m are only partially unzipped by using 500% KMnO₄. This is probably due to the large length to diameter ratio in the MWNTs. The peak at $2\theta \sim 10^\circ$ in the XRD pattern, corresponding to an interlayer spacing of 9.1 Å, (Fig. 1a) indicates the formation of unzipped graphene oxide nanoribbons¹¹ but a second peak at 2θ ca. 23°, corresponding to an interlayer spacing of 3.6 Å, indicates that there are still closed tubes or closed segments of

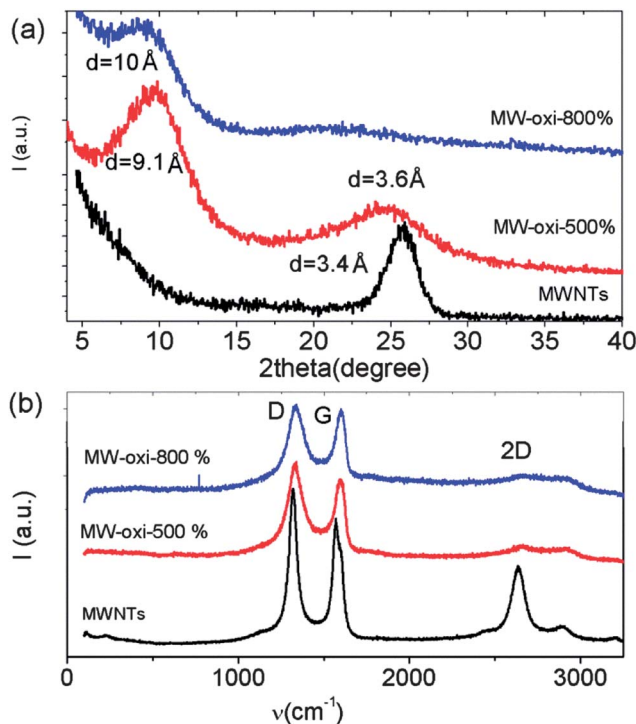


Fig. 1 (a) XRD patterns of initial MWNTs, the resulting graphene oxide nanoribbons after oxidation with 500 wt% and 800 wt% KMnO_4 in H_2SO_4 before annealing (b) Raman spectra showing shifts in the region of the D, G and 2D bands for the same samples.

tubes. However, when 800–850% of oxidant is used, the diffraction maximum corresponding to the interwall distance in carbon nanotubes completely disappears, indicating complete opening of the tubes (Fig. 1a).

In the case of FWNTs having one to four walls, and lengths up to 3 μm , the intensity of the reflections is low due to a reduced number of stacked layers. Nevertheless, XRD indicates that 500–700 wt% of oxidant lead to longitudinal opening of the FWNT to form nanoribbons (Fig. S1,† ESI). Due to the very high aspect ratio of the FWNTs, a large amount of oxidant in this range ensures complete unzipping, whereas a smaller percent oxidant in this range results in only partial unzipping. We have tried unzipping several commercially available MWNTs and have found that not all MWNT can be unzipped using our range of reaction conditions. In some instances the MWNT sample degrades to the point of dispersibility in the oxidizing solution instead of providing evidence of MWNT unzipping to produce high-aspect-ratio graphene oxide nanoribbons.

Raman analysis shows that the starting MWNT have sufficient defect concentrations to produce a high D/G intensity ratio (Fig. 1b and S1†). Moreover, oxidation conditions that produce essentially complete unzipping introduce more disorder, as measured by an increased D/G ratio. A high D/G ratio, like typically found for chemically modified graphene nanoribbons,¹¹ remains after thermal reduction of the graphene oxide nanoribbons although the relative intensity of the D vs. the G band is slightly decreased for both MWGNr and FWGNr (Fig. S2†).

Unzipped MWNTs

Powder XRD confirms the unzipping of the nanotubes by indicating a nearly 3 fold increase of the inter-layer distance during oxidation. Thermal reduction of the oxidized nanoribbons at 1050 $^\circ\text{C}$ shows the reappearance of an X-ray diffraction peak at about 3.5 $\text{\AA}$.

TEM has been used to further characterize the graphene nanoribbons obtained by thermal annealing of the oxidized nanoribbons. In conjunction with the appearance of a XRD reflection at 3.5 $\text{\AA}$ due to the inter-planar spacing due to graphene ribbon stacking, about the same interplanar spacing is seen in TEM (Fig. 2b) on the lateral edges of these stacked ribbons.

When imaged at low magnification in the TEM (Fig. 2a) the graphene ribbons show very high aspect ratios, due to several tens of micron lengths and few nanometers widths. Though ribbon lengths are much shorter than for the original nanotubes (300 μm), the nanoribbon aspect ratio is as high as 500.

In fact, looking at the TEM image of Fig. 2b gives the impression that the fibers are still MWNT. XRD, which is a bulk technique, confirms though, that all of the MWNT have been unzipped.¹¹ Fig. 2b shows a HRTEM image of a graphene ribbon from unzipping MWNTs after reduction through annealing at 1050 $^\circ\text{C}$. It is possible to observe the presence of carbonaceous adsorbates contaminating the surface—always present in reduced graphene oxide¹⁰—as well as an irregular layer termination, the result of the uneven oxidation process of unzipping. A comparison of the edges of the initial MWNTs, with that of the unzipped MLGNs before and after annealing is shown in Fig. S3.†

On the ribbon of Fig. 2c and d, which image two adjacent parts of the same nanoribbon that had been annealed at 1300 $^\circ\text{C}$, each of the graphene layers have a different edge termination as indicated by white arrows. Also in the majority of areas the separation between layers is approx. 3.5 $\text{\AA}$. This value is similar to the interwall distance in carbon nanotubes. Therefore, for such narrow graphene nanoribbons which still have very large aspect ratio, it is not possible to distinguish at first sight between the TEM image of a MWNT and that of a narrow graphene nanoribbon resulting from unzipping and subsequent high temperature annealing unless defective areas in which the tube is not completely open, or areas such as that of Fig. 2c are imaged. Other than those areas, for both MWNTs and MLG nanoribbons, the edge is composed of lines of dark and white contrast corresponding to the separation between walls in carbon nanotubes or to that of curled or closed edges of graphene nanoribbons respectively.

On the one hand, it may seem intriguing to find that in the majority of multilayer graphene nanoribbons the separation between lines of dark contrast in the edge is very close to the 3.5 $\text{\AA}$ found in MWNT and only in certain areas have the edges become more separated. However, it has already been reported in the literature that folding in free standing monolayer and bilayer graphene²⁶ upscrolling of the layer edges in the case of multilayer graphene,²⁷ and even closure of two layers by chemical reaction of free edges under high temperature

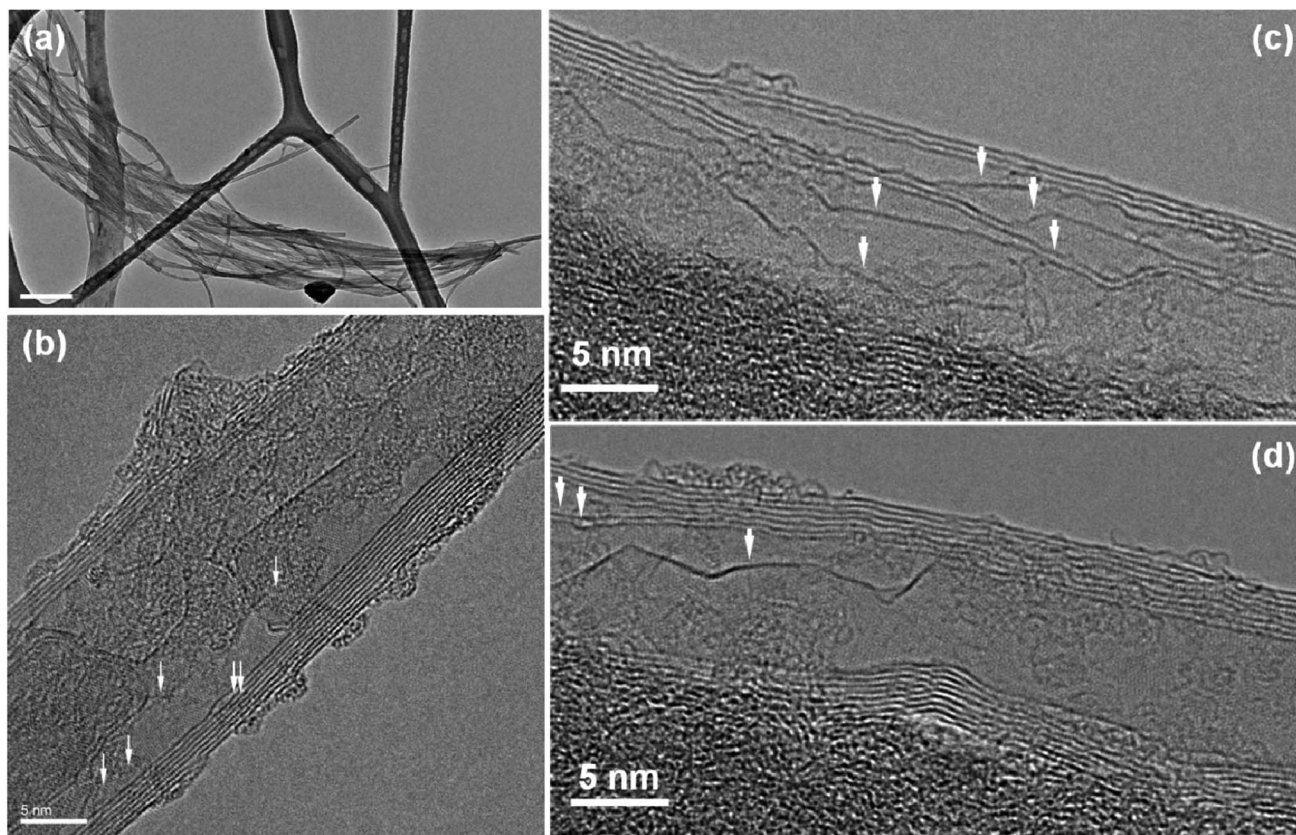


Fig. 2 (a) Low magnification TEM image of reduced graphene nanoribbon bundle obtained by unzipping MWNTs. (b–d) HRTEM images of the same narrow graphene ribbons (from the unzipping of a MWNT with 800% oxidant) after annealing in inert atmosphere at 1050 °C (b) and after annealing at 1300 °C. (c and d) Different edge terminations are indicated by white arrows.

annealing²² lead to the observation of straight edges with the observed contrast. This edge reconstruction to a nano-tube-like surface structure had also been observed in oxidized graphite and modelizations of the edge show that they occur in the nanosecond range at high temperature.²¹ This edge closure seems likely to be the reason for the near to 3.5 Å spacing found here in the edges of the nanoribbons.

Aiming for the complete exfoliation of the unzipped oxidized multilayer graphene into single layer graphene nanoribbon and in order to avoid the confusion created by the straight lines at 3.5 Å spacing in the edges of adjacent layers, we exfoliated the unzipped graphene oxide nanoribbons by sonication either in aqueous or organic (isopropanol based suspensions) dispersions with a tip sonicator, which has higher sonication power than the bath sonicator previously used. In this case along with the accomplishment of total exfoliation, nanoribbons were also cut in length.²⁸ For tip sonicated nanoribbons edge layering is not observed.¹⁶

Unzipped FWNTs

Edge layering is absent in the images of graphene nanoribbons obtained from unzipping of smaller diameter MWNT with few walls (SW, DW and TW). Comparing the TEM images of the starting FWNT (Fig. 3a and S4†) and that of the FWNTs after oxidative unzipping with 700% KMnO_4 (Fig. 3b) the latter show the absence of straight edges in the resulting unzipped

material. On the other hand, the non heated as unzipped oxidized material is too unstable to the electron beam and only amorphous ribbons can be observed. At low magnification it is possible to observe that the majority of materials are high aspect ratio nanoribbons (Fig. 3c).

We performed high temperature annealings both in argon atmosphere at 1050 °C (Fig. 3d) and under vacuum in a graphite furnace at 1400 °C (Fig. 4). Contrary to what was observed with graphene nanoribbons produced from unzipping of MWNT, the high temperature annealing produced the collapse and fission of individual nanoribbons. Macroscopically, the thermal treatment caused significant changes on the sample: the initially flat sheet or “buckypaper” self rolled into a few-millimeters diameter scroll. Likewise, microstructural changes also occurred. Fig. 3d show the majoritary morphology found when graphene oxide nanoribbons derived from FWNT were heated to 1050 °C in argon atmosphere. Small aggregates of microcrystalline particles grouped to form the star like balls of Fig. 3d and S5.† We speculate that due to the large amount of oxidant used and the large concentration of functional groups present in the FLG oxide nanoribbons,¹⁶ when the FLG nanoribbons are thermally annealed in argon they can break into small pieces and some of them can self scroll and others re-aggregate.

Heating to higher temperatures of 1400 °C in a graphite furnace resulted in three different morphologies (Fig. 4a). Highly crystalline graphitic onions of similar size to the stars

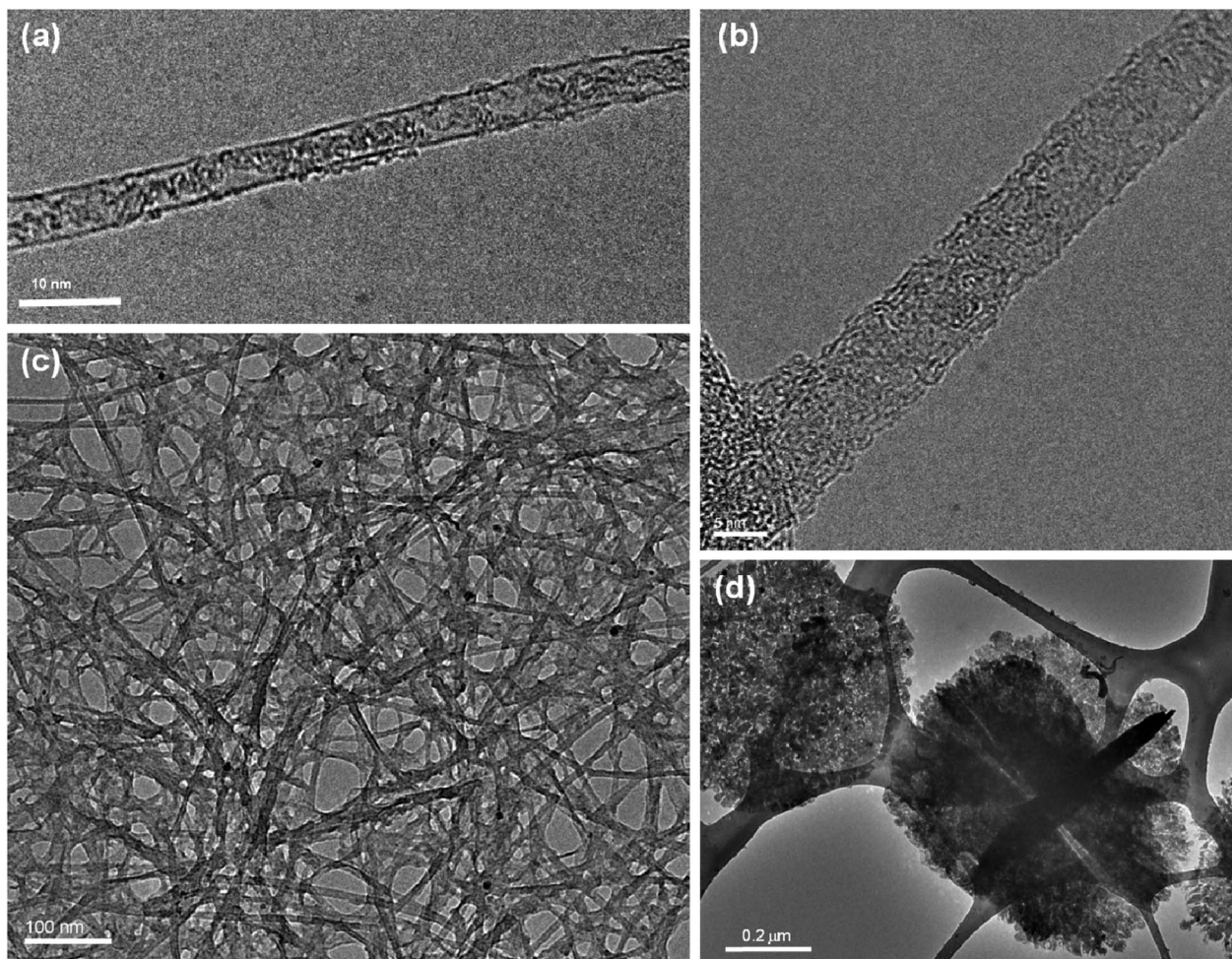


Fig. 3 (a) TEM image of a typical FWNT obtained by CVD (b) TEM image of a graphene nanoribbon obtained from unzipping of FWNT before high temperature annealing (c) low magnification image of the unzipped graphene nanoribbons showing the network of high aspect ratio ribbons. (d) Low magnification image of the same unzipped ribbons after annealing at 1050 °C in a quartz furnace under argon flow.

that were observed when annealed at 1050 °C. Thin graphene like foils of considerable larger size than the starting graphene nanoribbons and small solid particles that seem to be composed of microcrystals in an amorphous matrix similar to the microcrystalline particles that were observed when annealed at 1050 °C.

The graphene like flakes several microns wide show some stripes of different contrast that could be reminiscent of the original narrow nanoribbons (Fig. 4b). This fusion is probably due to the same kind of edge instability responsible for the interlayer closure in graphene nanoribbons derived from MWNT. However in the narrow ribbons derived from FWNT, since edge curling is required prior to edge closure, bonding with the adjacent ribbon might be more probable than self closure. The origin of the formation of these graphitic layers could be based on the same principle by which carbon adsorbates on top of graphene are transformed into a layer of amorphous carbon first and into crystalline graphene at temperatures above 1000 °C.²⁹

Fig. 4c show the fast fourier transform (FFT) of the image Fig. 4b showing a ring of 110 diffraction spots. This indicates

that small crystalline nanodomains compose the multilayer graphene flakes. The thickness of the flakes can be measured in a folded edge (Fig. 4e and S6†) as about 20–30 nm. Their FFT in Fig. 4f shows the 002 diffraction spots corresponding to the 3.4 Å interplanar spacings and the ring of 110 diffraction spots corresponding to the in plane 2.1 Å interatomic distances.

The other commonly found structure when the FLGs are annealed at high temperature are graphitic balls such as those detailed in Fig. 4g and h. Less than 10 nm in diameter graphitic nanoions are produced from high temperature annealing of nanodiamonds,³⁰ and 25–30 nm diameters can be produced by arc discharge in water.³¹ However the production of such large graphitic onions without any metallic core, has not been reported to date.

Finally, less structured particles (Fig. 4i) are found all over the TEM grids. These small pieces are composed of microcrystallites less than 5 nm in diameter within an amorphous matrix. This makes the annealed FLG nanoribbons a considerably more complex system to understand than the annealed MLG.

A general scheme summarizing the observed results is shown in Fig. 5. While the observed edge closure upon

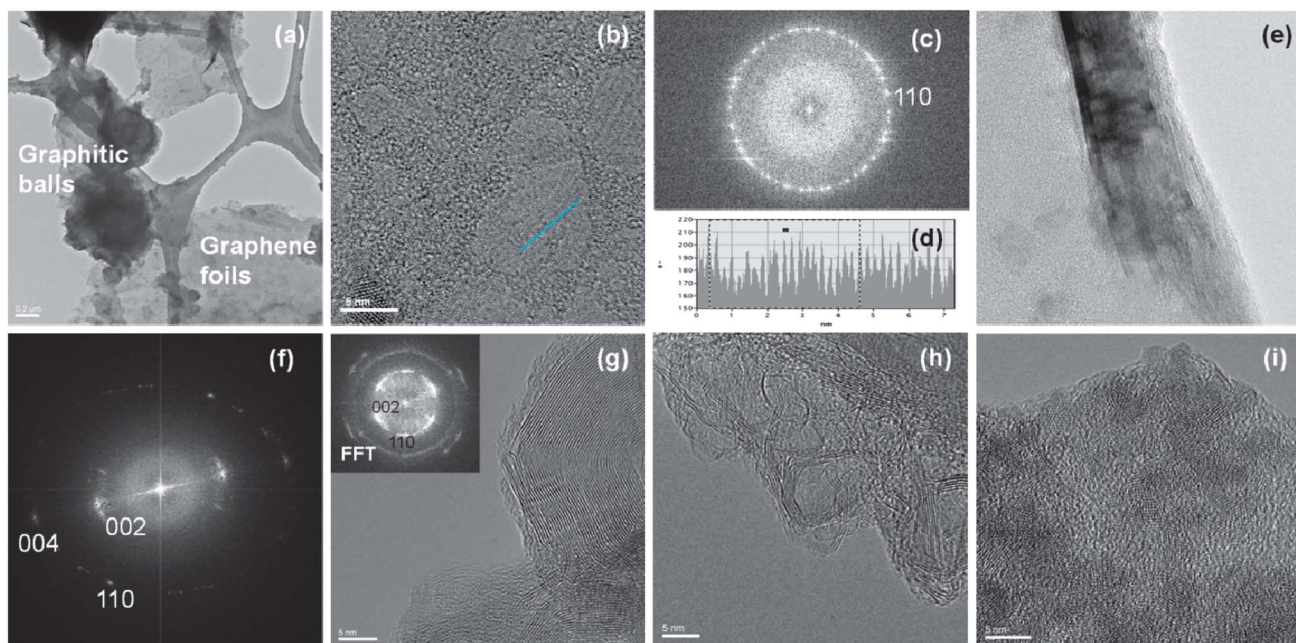


Fig. 4 (a) Low magnification TEM of carbon nanostructures formed after unzipping of FWNT and subsequent high temperature annealing at 1400 °C in a graphite furnace. (b) HRTEM detail of the graphene foils showing reminiscence of a hexagonal pattern in the plane (c) Fast Fourier Transform (FFT) of the image showing the presence of a ring of reflections at 2.1 Å (d) profile of intensities along the blue line of (b) showing the periodicity of 2.1 Å (e) folded edge of the graphene like foil showing about 40 layers with the 3.4 Å characteristic spacing along the c axis of graphite (f) FFT of (e) with the diffraction corresponding to the c axis on one direction and the spots corresponding to the in plane 2.1 Å spacings in different directions (g and h) HRTEM detail of the darker graphitic balls showing a d spacing of 3.4 Å between fringes inset in (f) is FFT (i) HRTEM detail of other smaller areas and in some cases the borders of the foils showing microcrystallites.

annealing MLG nanoribbons agrees with previous observations in graphene and graphite as well as with theoretical calculations, simulations are missing to explain the results found in FLG. Theoretical calculations that could explain the mechanisms that lead to the transformation of mainly uniform FLG into these 3 structure types—graphitic layers, graphitic balls and microcrystallites embedded in an amorphous matrix—seem necessary.

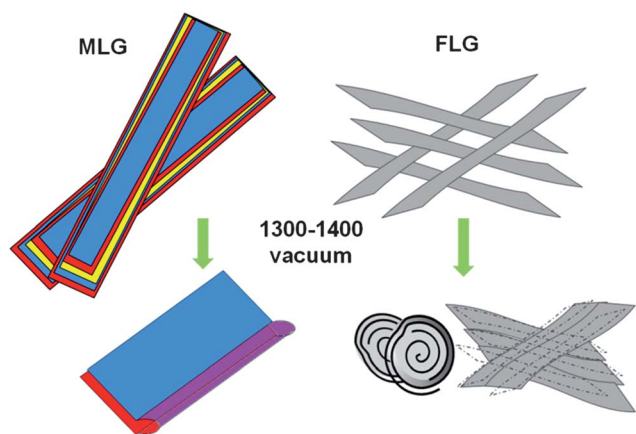


Fig. 5 Schematic representation of the edge closure process that occur in Multi layer graphene nanoribbons (MLG) and the self scrolling to yield graphitic onions and coalescence to yield large graphene foils of few layer (1–3) graphene nanoribbons (FLG) when the material is annealed in vacuum at 1300–1400 °C.

Conclusions

In conclusion, bucky-paper like samples of high aspect ratio MLG and FLG oxide nanoribbons can be prepared from oxidative unzipping of high aspect ratio multi walled and few walled carbon nanotubes respectively. These nanoribbons undergo very different structural changes when annealed at high temperatures. While MLG tend to curl up and close the edges forming stacked folded graphene or flattened nanotube like ribbons, the FLG nanoribbons tend to fuse and aggregate into different structures forming 3 types of carbonaceous nanostructures: 50–100 nm diameter crystalline graphitic balls, 20–30 nm thick graphitic foils as well as small microcrystalline-amorphous composite nanoparticles. These observations are of high importance for the application of the produced graphene oxide nanoribbons in electrodes and devices that require high temperature annealing. Theoretical efforts are still needed to understand the changes undergone by the FLG derived nanoribbons.

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