

Defect Nano-Engineering in Graphitic Materials: From Doped Carbons to Graphene

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In this talk, defects within graphite and carbon nanotubes will be categorized in 5 different groups: 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 non-hexagonal rings (e.g. pentagons, heptagons, or octagons); 2) *Topological defects*, occurring on the nanotube surface, which do not result in large curvature distortions of the tubule. In particular, these defects could be 5-7 pairs embedded in the hexagonal network or Stone-Wales (SW-type) defects that could be created by rotating a carbon bond within 4 neighboring hexagons, thus resulting in the transformation of 2 pentagons and 2 heptagons; 3) *Doping-induced defects*, arising from substitutional non-carbon atoms embedded (or incorporated) into the tubular lattice, 4) *Non- sp^2 carbon defects or edge-sites* caused 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), add-atoms and vacancies, and 5) *Folded (or highly strained) graphene*, caused by the severe deformation of the sheets, which induces reactivity by the deformations of the sp^2 hybridized atoms.

This presentation will review recent work related to different techniques used to identify defects using HRTEM, scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), Raman spectroscopy (RS), atomic force microscopy (AFM), thermogravimetric analyses (TGA), electron and thermal transport measurements, etc. It is important to mention that most of the time the presence of defects and their identification has been overlooked by numerous scientists. However these play a key role in the nanotubes' physico-chemical properties and biocompatibility. There are numerous challenges that will be discussed in this presentation: How do we identify defects efficiently? Could we distinguish among various defects? Would it be possible to establish a protocol able to quantify and control the amount of these defects? How many defects are necessary to fabricate robust polymer composites or 3D architectures? Could I introduce specific defects in order to make materials biocompatible? Could we promote ferromagnetism by introducing specific defects in nanostructures?, etc.

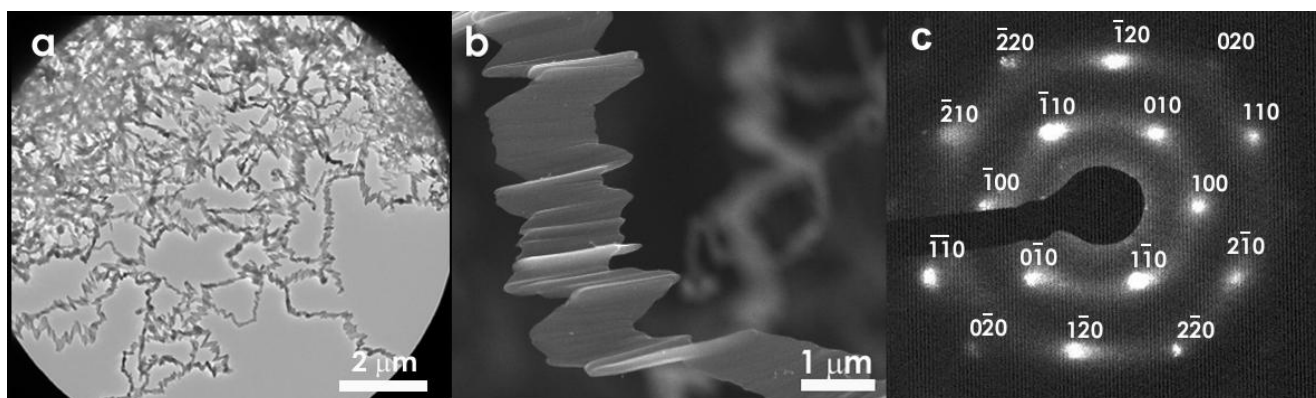


Fig. 1 (a) Low and high magnification TEM image of graphene nanoribbons; (b) SEM images of an individual graphene nanoribbons, and (c) indexed electron diffraction pattern of an individual thin graphene nanoribbon (ca. 10 nm thick) showing the ABAB... stacking of the graphite structure with a 3D order.

We will also describe the use of chemical vapor deposition (CVD) for the bulk production (grams per day) of long, thin and highly crystalline graphene ribbons (<20-30 μm in length) exhibiting widths of 20-300 nm, and small thicknesses (2-40 layers; Fig. 1). These layers usually exhibit ABAB... stacking as in graphite. We also carried out transport measurements on individual nanoribbons inside the HRTEM and performed Joule heating experiments that resulted in the generation of highly crystalline graphite nanoribbons.

Finally, we will describe different methods developed by our group to obtain graphene nanoribbons based on the unzipping of multi-walled carbon nanotubes (Fig. 2). It is clear that these methods offer a scalable route to graphene and graphitic nanoribbons. For multi-layered ribbons, exfoliation could be obtained (detachment of the layers into individual layers) as well as cutting into shorter pieces. It is clear that the ribbons and their exfoliated forms (containing several bare edges) could be used as gas storage devices, electronic wires, sensors, catalytic substrates, nanocircuits, etc. By using this new ribbon material, it is now possible to unveil new applications and novel physico-chemical properties associated with layered sp^2 hybridized carbon.

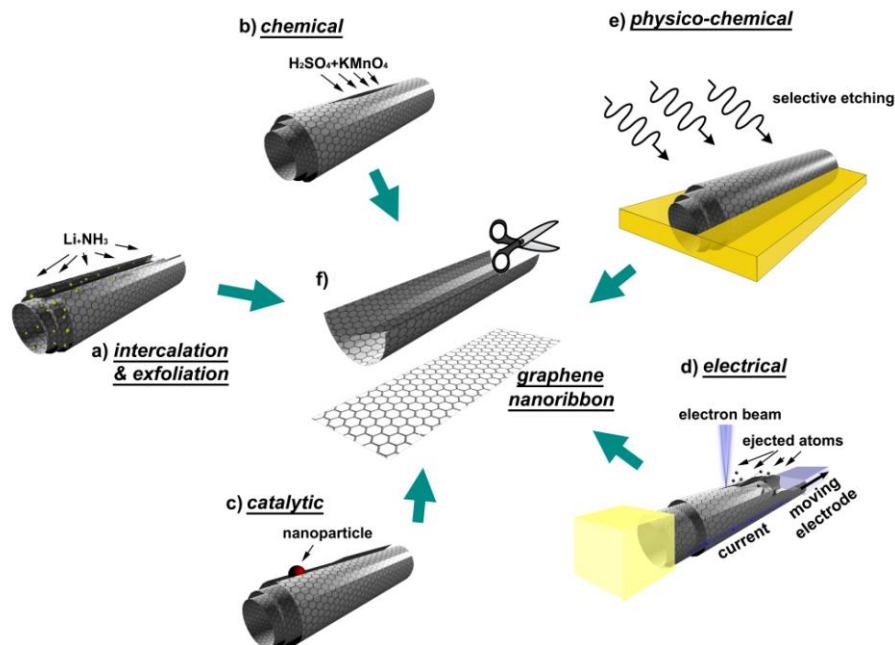


Fig. 2 Sketch showing the different ways nanotubes could be unzipped to yield graphene nanoribbons (GNRs): **(a)** intercalation-exfoliation of MWCNTs, involving treatments in liquid NH_3 and Li, and subsequent exfoliation using HCl and heat treatments; **(b)** chemical route, involving acid reactions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

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