Transformation of Carbon Nanotubes to Graphene Nanoribbons

Scientists at National Chemical Laboratory (CSIR-NCL), Pune have recently reported a new method of transforming carbon nanotubes (CNTs) to nanoribbons comprising a few layers of graphene. This was achieved electrochemically by the oxidation of CNTs at controlled potential, followed by reduction to form graphene nanoribbons (GNRs) having smooth edges and fewer defects. Such an “unzipping” of CNTs (single-walled, multi-walled) in the presence of an interfacial electric field provides unique advantages with respect to the orientation of CNTs, paving the way to many new applications enabling possible production of GNRs with controlled widths and fewer defects.

Graphene is a “one-atom-thick” planar sheet of carbon atoms, densely packed in a honeycomb lattice and has possible applications in nanoelectronics, supercapacitors, solar cells, and hydrogen storage. Graphene exhibits many exciting properties, such as room-temperature quantum Hall effect, long-range ballistic transport with ten times higher electron mobility than in silicon, availability of charge carriers that behave as mass-less relativistic quasi particles, and quantum confinement resulting in finite band gap and Coulomb blockade effects, which could be useful for making many novel, next generation electronic devices. However, in order to fully realize these properties and applications, a consistent, reliable, and inexpensive method for growing high-quality graphene layers in excellent yields is crucial, as the existence of residual defects will heavily impact their electronic properties, adversely affecting almost all of these applications.

Existing methods of graphene preparation have several major limitations. For example, preparations by mechanical cleavage, silicon carbide sublimation, solvothermal synthesis, chemical vapor deposition, and plasma etching suffer from limitations such as poor quality and yield of graphene ribbons, formation of over-oxidized and defective nanoribbons, substrate-dependent behaviour, and the difficulty of controlling both layer thickness and edge smoothness in a predictable manner. Hence, accurate control of the quality of graphene layers along with their preparation in good yields poses a challenge.

Prof. James M. Tour and team from Rice University, Texas, USA in one of the more successful approaches converted carbon nanotubes (CNTs) to graphene with the longitudinal unzipping, using a mixture of potassium permanganate and sulfuric acid, facilitating a large-scale preparation of graphene nanoribbons (GNRs). However, this method has several disadvantages, primarily related to the selection of strong oxidizing agents. The choice to use chemical oxidation itself has serious issues, like over-oxidation of edges creating defect sites which, in turn, hamper the electronic properties of graphene. More significantly, electron mobility and conductivity diminish with this treatment, and there
is also a possibility of evolution of explosive gases. In addition, the use of strong reducing agents causes several difficulties in controlling the layer thickness of graphene ribbons, along with disposal concerns. In comparison, electrochemical oxidation, demonstrated by Dr. Vijayamohanand* and his student Dhanraj Shinde from CSIR-NCL, has ensured accurate control of the degree and sites of oxidation (especially with controlled potential techniques) under ambient conditions; hence, this method is capable of providing more precise unzipping of nanotubes in comparison with chemical and plasma-based approaches.

Since CNTs are graphene sheets seamlessly rolled into concentric tubes, from a geometrical perspective it may be possible to transform CNTs to graphene by a longitudinal cutting of all C–C bonds along the tube axis. Many computational approaches have recently attempted to reveal the exact geometric steps as well as the energetics of the process of unzipping, despite ardent challenges, and all these suggest that it is possible, in principle, to open tubes by applying an appropriate electric field.

The CSIR-NCL team has proposed an unprecedented method for transforming CNTs to GNRs by using an electrochemical approach, with the unique advantage that it allows controlling the graphene layer thickness and orientation. The electrochemical approach is an effective way to modify electronic states by modulating the electric field (chemical potential) to change the Fermi level of the electrode materials. An interfacial electric field is expected to orient the CNTs in this method, and hence longitudinal unzipping is more likely with possible C–C cleavage initiated at topological defects having enough strain, rather than a random breakdown in chemical methods.

Dr Vijayamohanand says that large graphene sheets cannot be made in this way, since the size of the graphene is limited by the diameter of the multi-walled carbon nanotubes (MWCNTs). However, single, double and multiwalled carbon nanotubes, all can be opened by this uncanny approach which validates the generic utility of this approach as verified by collaborative support from Dr. Aslam's group in IIT-Mumbai.

This study opens new pathways for the preparation of high-quality graphene in good yield, and there are also profound implications for certain applications like field emission, fuel cells
and Li battery electrodes, where CNTs are continuously kept under an electric field, where the durability of these materials could be affected by this continuous transformation.

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For further reading: