Graphene

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Graphene from Molecules

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The creation of small and low-dimensional entities has always inspired materials scientists. Since the advent of nanotechnology in the mid-1980s, zero- and one-dimensional nanoobjects (particles, wires, and tubes) have been prepared and studied. It took longer till mechanically stable and free-standing two-dimensional nanoobjects were first introduced. In the mid-2000s, Geim and Novoselov demonstrated the fabrication of single layers of carbon, in other words graphene, by the mechanical exfoliation of graphite with the help of "scotch tape".[1,2] Since then, physicists, chemists, and engineers have explored graphene intensively. Its unique electronic, mechanical, and optical properties give fascinating insights into two-dimensional systems and may eventually lead to innovative technology. This was acknowledged when the 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for *"groundbreaking experiments regarding the two-dimensional material graphene"*. Currently, the Web of Science lists over 10000 publications with "graphene" in their titles, and otherwise penny-pinching funding agencies celebrate spending records in connection with graphene research.

For an economical use of graphene in technological applications, one needs methods for processing and incorporating graphene into devices, and more important, highly efficient syntheses to produce high-quality graphene in industrial quantities. The pioneering production path, mechanical exfoliation, yields flakes of high quality, but this technique is not adequate for large-scale production. So, alternative strategies for graphene fabrication have been explored, among them the reduction of graphene oxide and the thermal decomposition of silicon carbide. A quite promising production method is the catalytic decomposition of chemical-vapor-deposited (CVD) organic molecules on transition-metal surfaces. It was found that copper surfaces are particularly capable of decomposing a diversity of organic material, which was emphasized in a recent publication with the striking title: "*Growth of Graphene from Food, Insects, and Waste*".[3] Although it would be a pleasant prospect to see future electronics built from recycled organic waste, a "large-scale" production based on CVD processes also has drawbacks. For example, in order to grow homogeneous graphene sheets the catalyst's surface should be free of defects. The polycrystalline foils currently used to produce graphene have thicknesses ranging from single to several layers and it is hard to imagine how single-crystalline foils can be used in mass fabrication.

There are promising chemical and synthetic approaches towards the large-scale production of graphene. As a direct "*two-dimensional polymerization of graphene-like structures from simple monomers, is still a challenge for carbon chemists*",[4] most molecular fabrication schemes attempt to reach the goal in two steps: first an extended two-dimensional "carbon sheet" is formed from organic molecules; then the carbon sheet is heated in vacuum (pyrolysis) to temperatures above 800 °C until it is transformed into graphene (Figure 1).

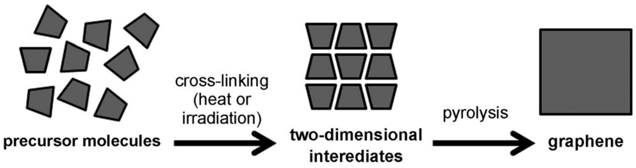

Figure 1. A molecular path towards graphene production: Precursor molecules are cross-linked to form two-dimensional intermediates. Pyrolysis transforms the intermediates into graphene.

In a pioneering effort, Turchanin et al. showed that self-assembled monolayers of biphenyls can be dehydrogenated and cross-linked by electron irradiation to form carbon nanomembranes (CNMs); subsequent pyrolysis then transforms the CNMs into homogeneous sheets of nanocrystalline graphene.[5] The thickness of the produced graphene is determined by the amount of carbon in the precursor molecules; hence, if monolayers of small molecules are utilized, multilayers cannot form. In closely related approaches[6] graphene nanoribbons were produced from adsorbed aromatic molecules. The nanoribbons undergo a sequence of thermally induced dehalogenation and dehydrogenation steps[6] until carbon–carbon bonds form between adjacent molecules, transforming the molecular assembly into a graphene ribbon. As in the case of cross-linked self-assembled monolayers, the molecular arrangement on a surface is essential to bring neighboring molecules into proximity such that they can react to form a two-dimensional carbonaceous entity. Once this is achieved, only moderate thermal energy is enough to link the molecules to form a graphene ribbon.

Now, Li et al.[4] move much further along this outlined path of making graphene from molecules. They demonstrate

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that the thermal condensation of dicyandiamide and glucose creates layered stacks of carbon nitride sheets that are transformed into graphene multilayers when pyrolyzed. The graphene multilayers can then be exfoliated to provide graphene sheets by a simple ultrasonic treatment. The advantage for the fabrication of large quantities of graphene is obvious: Li et al. produce their two-dimensional intermediates without the help of a catalyst or ionizing irradiation to promote the reaction between molecules and, more importantly, their reaction does not rely on a surface to guide the molecules into the required two-dimensional geometry. This is a tremendous advantage over other graphene fabrication schemes. The intermediate graphene precursor is produced in a bulk chemical reaction and the quantities produced are not dictated by the limitations of surface reactions. The produced graphene is nanocrystalline, that is, the single-crystalline domains have extensions of a few nanometers. Thus the conductivity is slightly lower than that of exfoliated graphene. On the positive side, a molecular preparation of graphene allows a much better "tuning" of the produced material by the appropriate choice of precursor molecules. For example, one can easily incorporate dopants, such as nitrogen, boron, and phosphorus, into graphene by choosing appropriate precursor molecules.

Finally, it is noteworthy that in recent years several two-dimensional carbon sheets have been described in the literature and a number of methods, surface-guided or not surface-guided, have been applied to produce them.[7–9] It is highly likely that most of these two-dimensional materials will also transform into graphene when pyrolyzed. In bulk carbon, graphite (sp^2) is the energetically most stable carbon allotrope; it is thus plausible to expect that sp^2-hybridized carbon atoms make up the energetically stable form of two-dimensional carbon. Thus pyrolysis, if applied wisely, should convert almost any thin and two-dimensional carbonaceous object into graphene, opening a promising path towards the mass production of graphene.

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