

FROM ZERO-DIMENSIONAL TO 2-DIMENSIONAL CARBON NANOMATERIALS - part II: GRAPHENE

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Abstract: *As was presented in the first part of this review paper, lately, many theoretical and experimental studies have been carried out to develop one of the most interesting aspects of the science and nanotechnology which is called carbon-related nanomaterials. In this review paper are presented some of the most exciting and important developments in the synthesis, properties, and applications of low-dimensional carbon nanomaterials. In this part of the paper are presented the synthesis techniques used to produce the two-dimensional carbon nanomaterials (including graphene), and also the most important properties and potential applications of graphene.*

Keywords: graphene, carbon nanomaterials (CNs), synthesis techniques.

1. INTRODUCTION- 2D-GRAPHENE

Graphene is a 2-dimensional network of carbon atoms. These carbon atoms are bound within the plane by strong bonds into a honeycomb array comprised of six-membered rings. By stacking of these layers on top of each other, the well known 3-dimensional graphite crystal is formed. Thus, graphene is nothing else than a single graphite layer (figure 1).

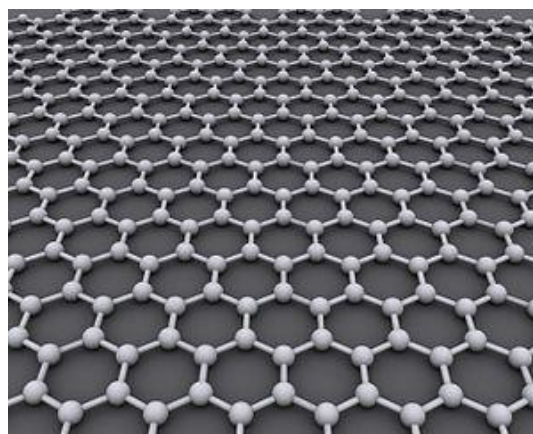


Figure 1. Graphene – 1 layer graphite

Until now graphene of sufficient quality has only been produced in the form of small flakes of tiny fractions of a millimeter, using painstaking methods such as peeling layers off graphite crystals with sticky tape. Producing useable electronics requires much larger areas of material to be grown. This project saw researchers, for the first time, produce and successfully operate a large number of electronic devices from a sizable area of graphene layers (approximately 50 mm²). The graphene sample, was produced epitaxially - a process of growing one crystal layer on another - on silicon carbide. Having such a significant sample not only proves that it can be done in a practical, scalable way, but also allowed the scientists to better understand important properties [1] [2].

2. GRAPHENE – OBTAINING METHODS

Until 2004 [3], as described in previous part of this paper, a physicists group led by Andre Geim and Kostya Novoselov from Manchester University, UK used mechanical exfoliation approach to obtain graphene. The discovery of isolated graphene monolayer has attracted wide attention to investigate the properties of this new yet ancient two-dimensional carbon nanomaterial due to its exceptional electronic and mechanical properties. More and more simple methods were searched for the growth of graphene. Several typical methods have been developed and reviewed as follows.

2.1. Mechanical Exfoliation

As mentioned above, [3] graphene flakes (figure 2) were first produced by continuously cleaving a bulk graphite crystal with a common adhesive tape and then transferred the thinned down graphite onto a cleaned oxidized silicon wafer substrate with visible color. The technique started with three-dimensional graphite and extracted a single sheet (a monolayer of atoms) called mechanical exfoliation or micromechanical cleavage.

Until now, mechanical exfoliation of graphite is still the best method to provide a small amount of high-quality samples for the study of a variety of graphene properties. Furthermore, the venerable technique has been used easily to obtain large size (up to 100 μm), high-quality, two-dimensional graphene crystallites, which immediately brought enormous experimental researches [4]. Meanwhile, modified techniques are needed to provide a high yield of graphene for industrial production.

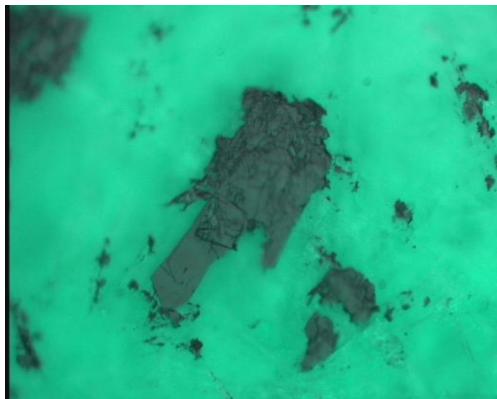


Figure 2. Graphene flakes

2.2. Epitaxial Growth

Recently, graphene was obtained by the epitaxial growth of graphene layers on metal carbides using thermal desorption of metal atoms from the carbides surface, or directly on metal surfaces by *chemical vapor deposition* (CVD). The typical carbide is SiC [5]; silicon carbide heated to very high temperatures leads to evaporation of Si and the reformation of graphite; the control of sublimation results in a very thin graphene coatings over the entire surface of SiC wafers, which initially showed more performances than devices made from exfoliated graphene.

So far, all of known synthesis approaches, however, are required in specialized laboratories for graphene sheets whose electronic properties are often altered by interactions with substrate materials. The development of graphene required an economical fabrication method compatible with mass production. The latest modified method was demonstrated by Aristov et al. [6] (figure 3). Based on their work, for the first time, graphene was synthesized commercially on available cubic β -SiC/Si substrates, which was a simple and cheap procedure to obtain industrial mass production graphene, which meets the need of technological application. Moreover, many other types of carbide have been exploited to produce supported graphene, such as TiC and TaC. It is well proved that metal surfaces can efficiently catalyze decomposition of hydrocarbons into graphitic materials to support growth of graphene on metallic surfaces by CVD. The advantage of epitaxial growth is large-scale area, but it is difficult to control morphology, adsorption energy, and high-temperature process.

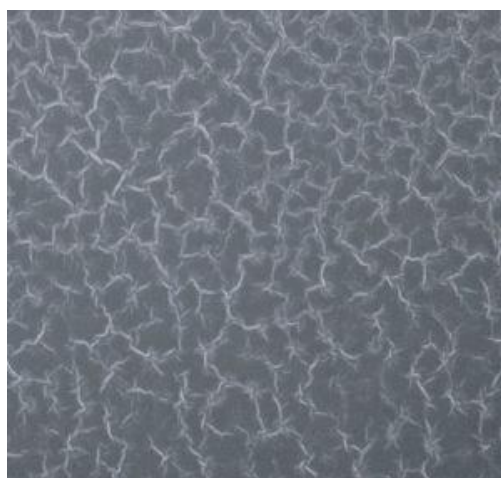


Figure 3: Edge-functionalized graphene deposited on a silica substrate

2.3. Chemical Exfoliation

The theory of chemical exfoliation is to insert reactants in the interlayer space for weakening the van der Waals cohesion. At first, the graphite flakes are forced upon oxidative intercalation of potassium chlorate in concentrated sulphuric and nitric acid, received carbon sheets with hydroxyl and carboxyl moieties. The suspension is known as graphite oxide (GO). The GO is highly dispersible in water, and it can be easily deposited onto SiO₂ substrates (figure 4).

The precipitate of GO is sonicated to form separated graphene oxide sheet, then another reduction, and finally graphene sheet is formed. When KClO₃ is used, it generates a lot of chlorine dioxide gas and emits a great deal of heat, so the mixture is highly hazardous [7]. Later was reported a modified method which was much faster and safer. Based on the technique introduced by them, graphite is dispersed into a mixture of concentrated sulfuric acid, sodium nitrate, and potassium permanganate in contrast to KClO₃. Meanwhile, Chen et al. [8] successfully achieved thermal reduction of graphene oxide (GO) to graphene with the assistance of microwaves in a mixed solution of N, N-dimethylacetamide, and water (DMAc/H₂O). The reduction of GO can be accomplished rapidly and mildly.

This method is rapid, not requiring any solvents or stabilizers, inexpensive, and easy to scale up.

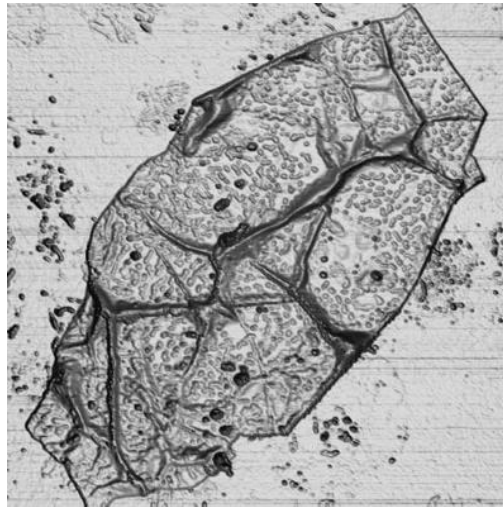


Figure 4. Chemically exfoliated graphene

3. PROPERTIES AND APPLICATIONS OF CNs

There are several various allotropes of carbon such as graphite, diamond, and amorphous carbon. Therefore, the physical and mechanical properties of carbon strongly depended on the allotropic forms of carbon. As an example for the mechanical property of hardness, diamond is known as one of the hardest materials, while graphite is soft enough to be used for making pencils. About the property of color, diamond is considered transparent while graphite is an opaque material and black. As another example, while graphite is a good conductor, diamond just demonstrates a low electrical conductivity. On the other hand, diamond is normally known as a highly thermal conductive, while graphite is considered as the most thermodynamically stable material.

3.1. Graphene

In 2007, Meyer et al. [9] used *transmission electron microscopy* (TEM) to study the atomic structure of a single-layer graphene. As they reported, they have studied individual graphene sheets freely suspended on a microfabricated scaffold in vacuum or the air. The membranes were only one-atom thick, yet they still displayed long-range crystalline order. According to their studies using TEM, the suspended graphene sheets are not perfectly flat. In other words, the suspended graphenes were observed as rippling of the flat sheet, with amplitude of about 1 nm. As the authors explained, the atomically thin single-crystal membranes offered ample scope for fundamental research and new technologies, whereas the observed corrugations in the third dimension may provide subtle reasons for the stability of two-dimensional crystals.

3.2. Mobility of Graphene and the applications

Graphene is known as a high electron mobility material at room temperature, so that the reported value is $15,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. In 2005, Novoselov et al. [10] considered graphene as a condensed-matter system in which electron transport is essentially governed by Dirac's (relativistic) equation. In 2008, Morozov et al. [11] studied temperature dependences of electron transport in graphene and showed that the electron mobility higher than $2 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is achievable if extrinsic disorder is eliminated. In the same year, Chen et al. [12] studied the intrinsic and extrinsic performance limits of graphene devices on SiO_2 . According to the studies mentioned above, it seems that the electron mobility in graphene should be almost independent of the temperature between 10 K and 100 K.

Due to the high mobility of graphene, this material is known as a promising nanomaterial particularly for those applications in which transistors need to switch extremely fast. Furthermore, the high mobility of graphene involves this material in the applications related to chemical and biochemical sensing.

On the other hand, the resistivity of the graphene sheets is $10^{-6} \Omega \text{ cm}$ which is less than the resistivity of silver as known as the lowest resistivity at room temperature. Such a unique low resistivity and also the very low thickness of graphene have made this material to have a great role in many applications such as mechanical fields, electrical conducting, and transparent films which are necessarily applicable in the field of electronics such as producing touch screens and photovoltaic cells.

4. CONCLUSIONS

As described in this paper, the unique structure and properties of low-dimensional carbon nanomaterials as the advanced materials have led them to have a strong and important potential role in various scientific fields and engineering such as nanoscale electronic devices, field emission displays, diodes, transistors, sensors, composite polymers, artificial muscles, mechanical reinforcements, capacitors, and hydrogen storage. For example, carbon nanobuds are the recently produced materials from two previously known allotropes of carbon nanotubes and fullerenes. These fullerene-like “buds” have found the unique properties of both fullerenes and CNTs which have many applications as good field emitters as well as their role to improve the mechanical properties of composites. As another example, the application of CNTs to develop the biofuel products is being noticeably growing due to their strongly deferent properties comparing to the previous products.

As a matter of fact, due to the unique mechanical, optical, and electronic properties of carbon nanotubes, the publication statistics show that CNTs have succeeded to attract the main body of the authors' interest since 1991 up to now. However, as described in this paper, carbon nanomaterials are not limited to CNTs. Therefore, the future outlook of applications of these materials depends on the capability of the use of each one. As an interesting bioapplication example, nanodiamonds may be capable to be used for biolistic delivery in gene therapy, drug delivery, and vaccines as a solid support matrix. Furthermore, there is a strong possibility in near future to use nanodiamonds in the medical immunoassays as either the detection tag or the solid support matrix [13].

As the definition of the low-dimensional carbon nanomaterial, these materials also cover a wide range of carbon-related nanostructures such as nanodiamonds, fibers, cones, scrolls, whiskers, and graphite polyhedral crystals. In fact, there are expectable outlooks for the use of these materials in the fields of molecular electronics, sensing, nanoelectromechanic devices, field-emission displays, energy storage, and composite materials, as well as their growing applications in medical science, health, and daily life [14].

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