# Production methods of graphene and resulting material properties

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*Graphene, a monolayer form of carbon with a two-dimensional honeycomb lattice, has shown many interesting properties from the mechanical, electrical, thermal and optical point of view. These properties make graphene a material of interest for many applications, for example in the fields of electronics, composites, sensors as well as energy storage and conversion. These engineering applications require availability of graphene on the mass scale and thus the development of suitable processes is necessary.*

*Here, an overview of three production methods of interest, chemical vapour deposition (CVD), exfoliation of graphite oxide, and electrochemical synthesis route, is presented.*

## CVD Synthesis

Chemical vapour deposition (CVD) is in principle a process of thermal decomposition of hydrocarbons on transition metals [1]. Graphene growth occur due to the precipitation of graphite from carbon species within the Ni film the Ni film and the carbon atoms form a solid solution resulting in an ultrathin graphene film (1 to ~ 10 layers) over the Ni surface.

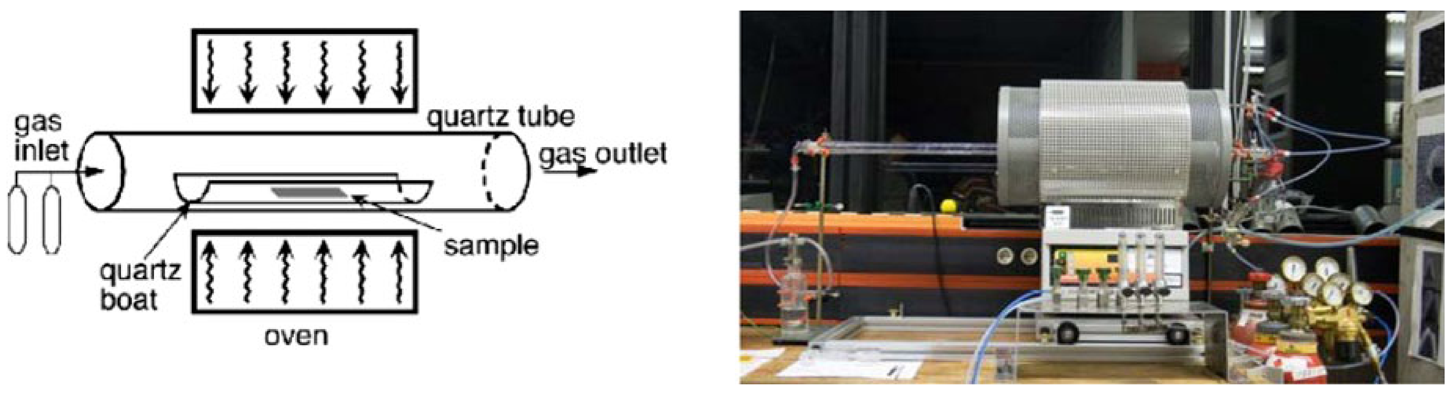
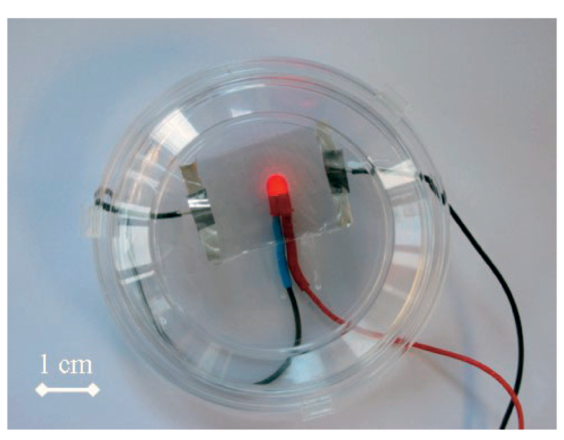



*Fig. 1*
*Schematic diagram of CVD reactor (left) and photo of an oven for carbon nanomaterials production (right).*

This method allows the transfer of the produced film to alternative substrates, in our case a polycarbonate (PC), by wet-etching the Ni film. This results in a free-standing PC/graphene membrane (Figure 2) that exhibits outstanding optical transparency and electrical conductivity.




The ability to grow single and few-layer graphene with CVD is an important advantage. This technique can potentially enable the simple growth of graphene at particular locations and with desired geometries by controlling the catalyst morphology and position [1].

*Fig. 2 Transparent and conductive coating made of graphene on polycarbonate with 70 % transmittance at 550 nm and 600 Ohm/ sq. Size: 2 x 3 cm².*

## Exfoliation of Graphite

Graphite oxide (GO) is produced by the oxidative treatment of graphite via one of three principal methods developed by Brodie [2], Hummers [3], and Staudenmeier [4]. GO consists of graphene sheets decorated mostly with epoxide and hydroxyl groups [5]. Rapid heating of GO results in its expansion and delamination caused by rapid evaporation of the intercalated water and evolution of gases from pyrolysis of the oxygen-containing functional groups. Such thermal treatment has recently been suggested to be capable of producing individual functionalized graphene sheets [6]. For a schematic representation of the graphite oxidation, exfoliation and reduction see Figure 3.

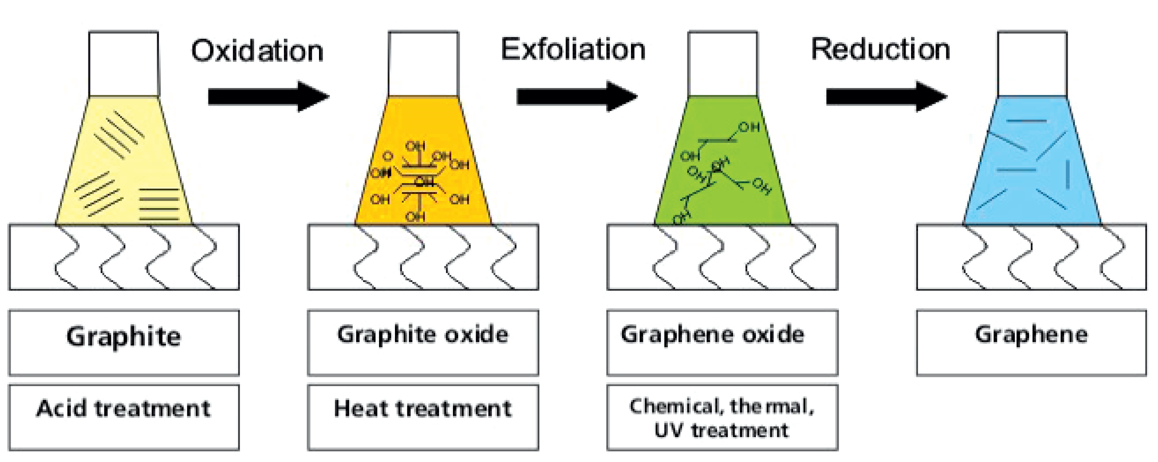



*Fig. 3*
*Schematic representation of graphite exfoliation process resulting in graphene (reduced graphene oxide).*

GO is electrically insulating and thermally unstable. Notably, it has been demonstrated that the electrical conductivity of GO can be restored by chemical reduction. The SEM images of reduced GO sheets are shown in Figure 4.

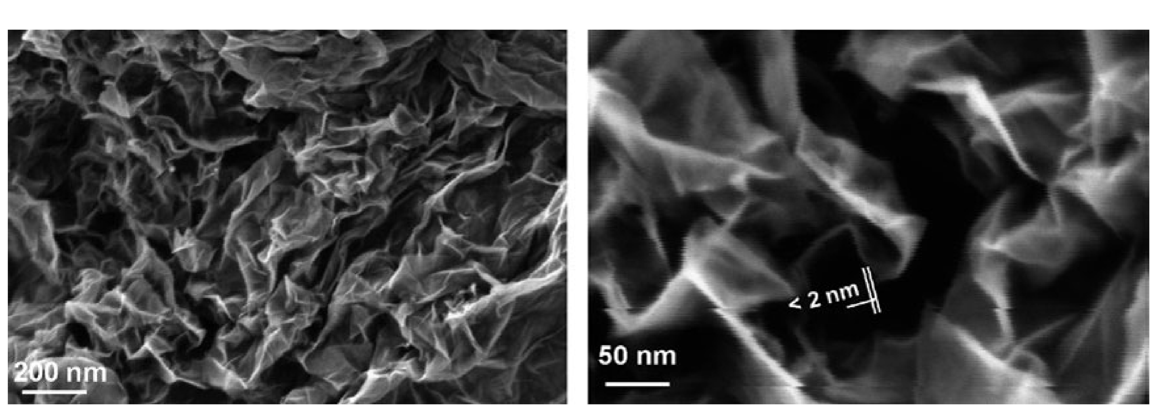



*Fig. 4*
*SEM image of aggregated reduced GO sheets (left) and a platelet having an upper bound thickness at a fold of ~ 2 nm (right) [5].*

This carbon-based material consists of thin graphene-based sheets and possesses high specific surface area and electrical conductivity.

## Electrochemical Synthesis

Electrochemical synthesis of graphene sheets is a one step treatment [7] and can be classified as subcategory of graphite exfoliation.

In this case, two high purity graphite rods are used as electrodes. In the electrochemical cell they are immersed in the electrolyte bath composed of ionic liquid and water. The schematic of the electrochemical cell and the photo of the experimental setup are shown in Figure 5 and Figure 6, respectively.

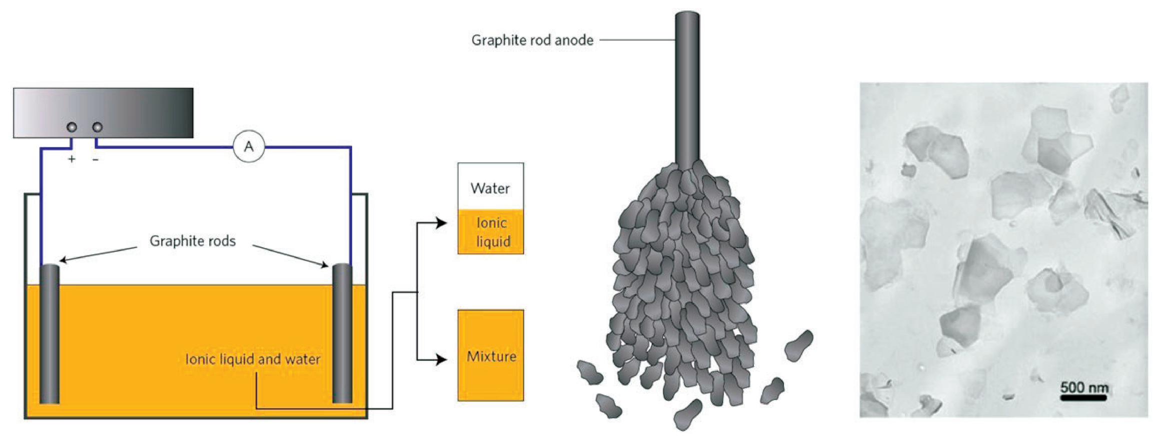



*Fig. 5*
*Left: experimental schematics [7];*
*middle: exfoliation of chemically modified graphene sheets from the graphite anode [7];*
*right: TEM image of resulting graphene material with width of 500 nm, length 700 nm and thickness of ~1,1 nm [7].).*

Static potential is applied to the two electrodes. Under these conditions the anode is corroding and a black precipitate is gradually appearing in the reactor. After electrolysis, stable graphene dispersion is obtained. The supernatant can be directly filtered to form a graphene paper, or washed and dried to obtain bulk powders of graphene [8]. In Figure 6 the filtered material is shown.

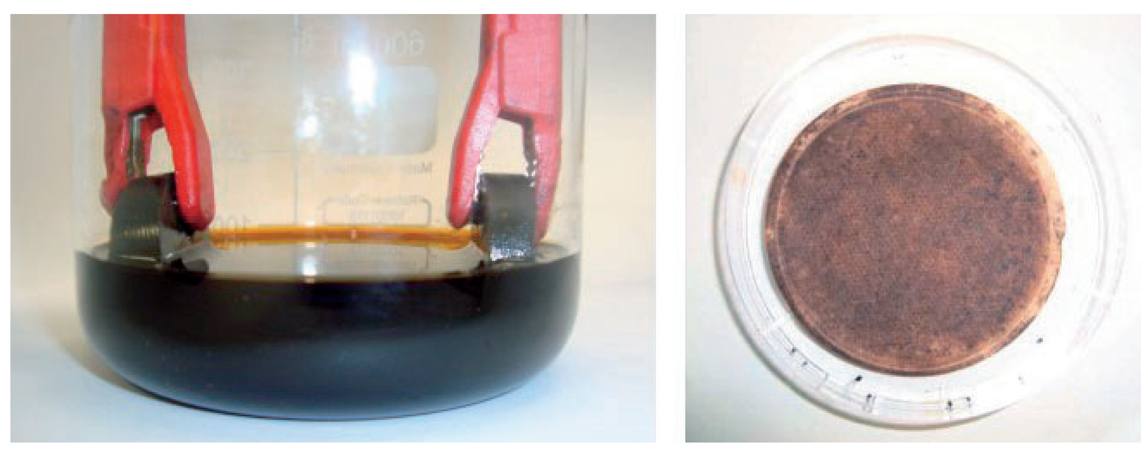


*Fig. 6*
*Left: Experimental setup for electrochemical production of graphene. Right: The product obtained after filtration of the electrolyte solution.*

The as-prepared graphene nanosheets are stable in aqueous solution, ready to be isolated as monolayer or multilayer graphene sheets.

## Properties Engineering

Properties of graphene can be further modified by post-synthesis treatment. For example, chemical impurities, atomic substitutions and functional groups can be an effective way to modify and control the properties of graphene. Furthermore, defects alter the electronic structure and therefore the properties.

Among properties engineering methods, one can find:

- Chemical functionalization – attachment of functional groups to the carbon atoms, influences chemical properties/compatibility with other materials, what may be of crucial importance in the production of composite materials.
- Substitutional functionalization – substitution of carbon atoms in the graphene structure with other atoms influences the electrictronic structure and properties of graphene important for application as electronic components.
- Inclusion of defects – deformation of graphene lattice structure by rearrangement of carbon atoms, influences optical properties of graphene, with the potential of improved transparency for applications in e.g. photovoltaics.

## Conclusions

- Chemical vapour deposition (CVD) allows fabrication of large area graphene films of single- to few-layer graphene in comparison with other methods and with exceptional electrical conductivity. However, the CVD process still has to be optimized to enable uniform growth of single-layer graphene. Furthermore patterning of the substrate will allow production of graphene with a specific form, a feature that cannot be controlled in graphite-exfoliation processes.
- Exfoliation of graphite is a cost efficient production method due to the price of raw materials. However, chemical processing inevitably introduces defects and functionalization in graphene sheets leading to the decrease of conductivity. Thus the main challenge for optimization of this process is to find routes for complete restoration of the sp2 carbon network of pristine graphene.
- Electrochemical synthesis under the assistance of ionic liquids is a green method for the synthesis of graphene sheets in comparison with chemical exfoliation of graphite as it does not make use of any environmentally unfriendly solvents. However, the high costs of ionic liquids make this process an expensive alternative to chemical exfoliation. Also in this process graphene is functionalized resulting in a material of higher compatibility with organic solvents and polymers. However the influence of this modification on other properties still has to be investigated.

***References***

*[1] A. Reina et al., »Large Area, Few-Layer Graphene Films on arbitrary Substrates by Chemical Vapor Deposition«, Nano Letters, Vol. 9, No. 1, 30-35 (2009)*
*[2] B.C. Brodie, »Sur le poids atomique du graphite«, Ann. Chim. Phys. 59, 466–472 (1860)*
*[3] W. Hummers, R. Offeman, »Preparation of graphitic oxide«, J. Am. Chem. Soc. 80, 1339 (1958)*
*[4] L. Staudenmaier, Verfahren zur Darstellung der Graphitsäure, Ber. Dtsch. Chem. Ges. 31, 1481–1499 (1898)*
*[5] S. Stankovich et al., »Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide«, Carbon 45, 1558 - 1565 (2007)*
*[6] H.C. Schniepp, J.-L. Li, M.J. McAllister, H. Sai, M. Herrera-Alonso, D.H. Adamson, »Functionalized single graphene sheets derived from splitting graphite oxide«, J. Phys. Chem. B 110 (17), 8535–8539 (2006)*
*[7] N. Liu et al., »One-Step Ionic-Liquid-Assisted Electrochemical Synthesis of Ionic-Liquid-Functionalized Graphene Sheets Directly from Graphite«, Adv. Funct. Mater. 18 (10), 1518-1525 (2008)*
*[8] G. Wang et al., »Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation«, Carbon 47, 3242-3246 (2009)*