

Wet Chemistry of Graphene

by Jenny Malig, Jan M. Englert, Andreas Hirsch, and Dirk M. Guldi

The 2010 Nobel Prize in Physics went to K. S. Novoselov and A. K. Geim for their ground-breaking work in the field of low dimensional carbon allotropes, namely graphene.

Graphite, the most abundant naturally occurring carbon allotrope, is considered the ancestor of low dimensional carbons.¹ Graphite crystals are composed of two dimensional sheets of sp²-hybridized, hexagonally arranged carbon atoms—so-called graphene—that are regularly stacked. It has been proposed as early as in ancient Greek literature that graphite, derived from the greek word *graphein* (to write), consist of such a layered structure. However, it was not until 1779 that graphite was shown to consist of carbon. The common perception was that graphite was a metal owing to its luster and noble appearance. In fact, this insight is reflected in the electronic properties of the graphite-building blocks, *i.e.*, graphene sheets, which are characterized as semi-metallic. In line with theoretical predictions, charge carriers in graphene were found to behave like mass-less Dirac fermions.² The latter is a direct consequence of the linear energy dispersion relation. Such a feature is currently the inception for a material that is poised to find its way into both low- and high-end technology applications.

Not surprisingly, numerous controversies emerged regarding the novelty and originality of the material as well as its initial discovery.³ For example, if we consider another low-dimensional carbon allotrope, namely carbon nanotubes, presumably the oldest published work dates back to the 1880s.⁴ To this end, the extraordinary stiffness of the Damascus sword has been attributed to the content of carbon nanotubes that are formed during the original method of producing Damascus steel. Nevertheless, characterization techniques were deemed necessary to be developed to establish unambiguous evidence for the presence of low-dimensional carbon. Implicit is, however, that a full comprehension of the material's potential was not possible during these early days.

The sheer exploding interest in low-dimensional carbon allotropes, in general, and graphene, in particular, is closely related to the massive demand for new nanocarbons with potential applications in areas such as electronics, energy conversion systems, etc. Thus, it is not surprising that the advent of fullerenes in 1985 and the dawn of the nanotechnology century triggered tremendous research activity in the field of carbon allotropes. These efforts were rounded off by the re-discovery of carbon nanotubes (CNTs) in 1991 and graphene in 2004 with both of them having huge potential to meet the demands of the market.

In stark contrast to the production methods of CNT—gaseous precursors at elevated temperatures (super growth, CVD, HiPco, CoMoCat), arc discharge, or laser ablation—the use of graphite as starting material for the top-down preparation of graphene offers a cost-efficient and environmentally-friendly alternative to low-dimensional nanocarbon. Unfortunately these benefits are tied to the necessity of overcoming the huge amount of crystal stacking energy stored in highly ordered graphite. When in van der Waals contact, graphene sheets are subjected to very efficient π - π stacking interactions. This, in fact, minimizes the surface energy. CNTs, on the other hand, due to their cylindrical geometry may only interact with a very limited contact area. Nevertheless, it is possible to move individual graphene sheets laterally to the crystal's stacking axis when shear forces are applied. This is the basis for graphite serving as a lubricant on an industrial scale. We may speculate that such considerations led to the initial idea of micromechanical cleavage of graphene sheets from highly-ordered pyrolytic graphite (HOPG) by sticky tape.²

Micromechanical exfoliation fails, however, for producing graphene in large quantities. This then calls for the necessity to develop alternative approaches. Actually, besides the aforementioned top-down approach, several bottom-up approaches have been shown to provide graphene with atomic precision. As demonstrated by Müllen *et al.*, organic chemistry offers the needed toolbox for preparing spherical oligophenyl dendrimers as precursor materials that cyclodehydrogenate to form planar *nano*-graphenes.⁵

In complementary work, *in situ* growth on transition metal substrates (*i.e.*, from solid or gaseous carbon sources) was recently explored as a versatile methodology to provide wafer scale, ultra large-area graphene.⁶ Finally, epitaxial growth of graphene films from SiC wafers should be mentioned, which, in turn, opens up ample opportunities for future semiconductor applications.⁷

Solution processing is, nevertheless, an indispensable prerequisite to meet demands in emerging fields such as printable electronics, etc. Having solutions ready at hand, enables chemical modification/functionalization, purification, and transferring graphene from the solution phase to every conceivable substrate by means of spin-, spray-, drop- or dip-casting. Likewise the Langmuir-Blodgett⁸ technique has been successfully implemented for cost-efficient ITO substitution in flexible transparent conductive photostable thin films. Overall, solution processing has graphene interacting with the solvent or other dissolved chemicals. To this end, control over the electronic structure of the single carbon sheets by either non-covalent or covalent chemistry has already put into effect. We wish to refer to the endless opportunities that rest on specific donor and acceptor functionalities that will become invaluable assets as soon as fine-tuning graphene in a controlled and reproducible fashion is achievable (Fig. 1).

The first success in dissolving graphite dates back to the end of the 19th century.⁹ In this work, treating graphite with strong acids—augmented by oxidation and heating—afforded products referred to as graphite acid, which is essentially graphite oxide. The resulting graphite oxide was found to swell once in contact with water—an indication for its hydrophilic nature.¹⁰ When heating to 1000°C, graphite oxide, which consists of graphene sheets decorated with numerous different oxygen containing functionalities (*i.e.*, carbonyls, carboxyls, epoxides, and alcohols) is subject to volume expansion.¹¹ Volatile products formed during the thermal decarboxylation of graphite oxide are trapped in the interlayer spacings and are responsible for the expansion—a procedure that resembles the thermal reduction of graphite oxide, which was known and studied since at least 1918.¹² Further removal of oxygen-containing functionalities on the surface requires chemical treatment with, for example, reducing agents (*i.e.*, hydrazine or NaBH₄),¹³ which impacts, however, the material's solubility in polar solvents. Notably, not a single procedure has yet been shown to fully restore the pristine hexagonal framework of the graphene lattice. Even supplying the carbon that has been lost during the decarboxylation/reduction in a final CVD step did not regenerate pristine graphene.¹⁴ In the literature, these materials are often described as chemically-derived graphene (CCG) or reduced graphene oxide (rGO). However, the resulting nanocarbons differ from graphene, since the structural integrity and hence the electronic properties are altered when compared to pristine graphene.¹⁵

Chemical modification/functionalization, which aims at activation and at better processability, includes intercalating graphite with strong electron donors (*i.e.*, alkali metals) or electron acceptors (*i.e.*, FeCl₃). The obtained products considered as graphite intercalation compounds (GICs).¹⁶

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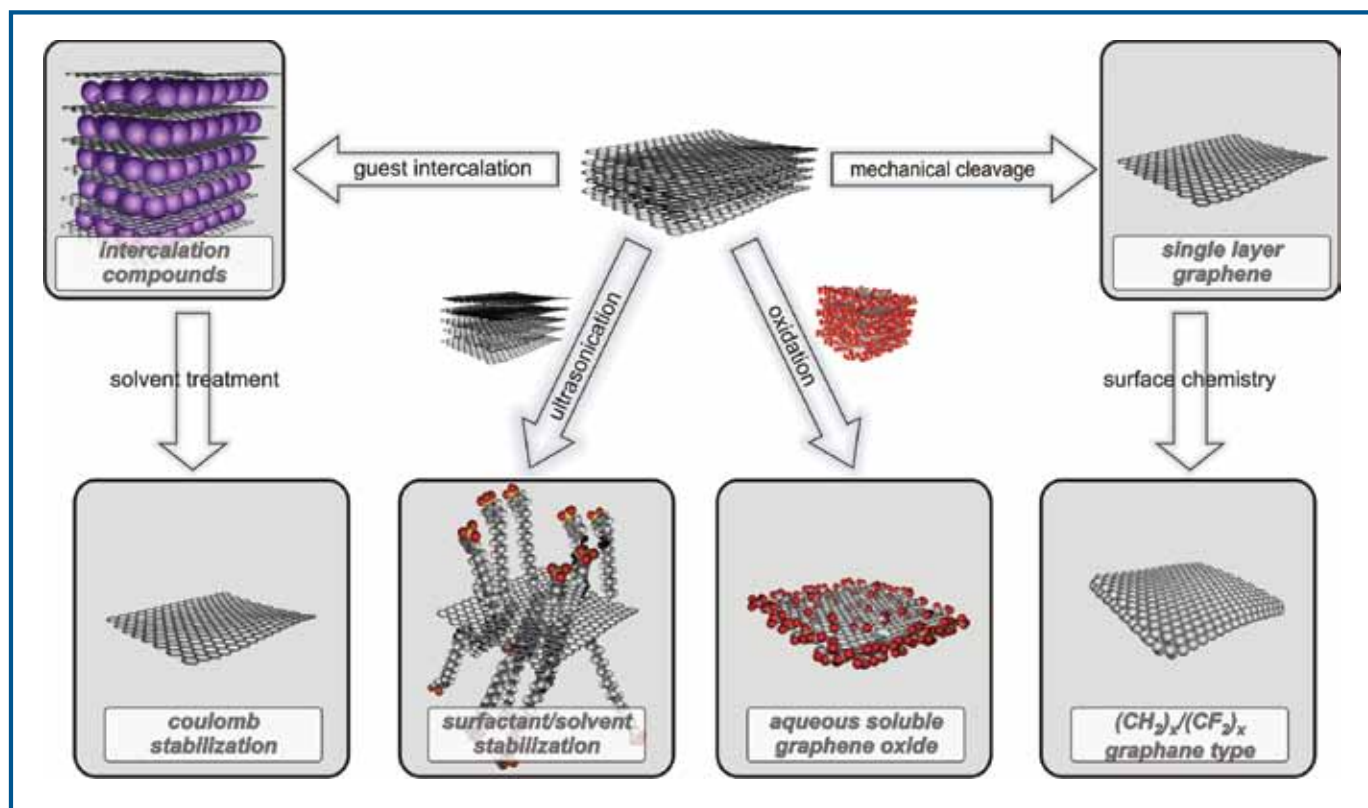


Fig. 1. Selected pathways towards wet chemically derived graphenes obtained from graphite as starting material.

GICs, which have been synthesized stoichiometrically, reveal highly-ordered crystal packing with alternating carbon and guest lattices. As a result of incorporating guests, the interlayer graphene distance is increased. This reduces *per se* the van der Waals forces, on one hand, and increases Coulomb forces, on the other hand. Coulomb interactions are introduced by charge transfer between the guest and graphene sheets and, in turn, lead to a partial ionic character. Owing to the strongly reducing conditions needed to form, for example, 1st stage potassium donor GICs, such graphite activation is limited to inert functional groups and solvents.¹⁷

The chemistry of CNTs has served as a unique test-bed for developing/establishing non covalent and covalent functionalization methodologies with nanocarbons (Fig. 2). These methodologies are partially applicable to graphite. Essential steps are activation and exfoliation of two dimensional graphene sheets, which are induced by, for example, ultrasound treatment prior to the functionalization. Ultrasound emerged, in this context, as a viable method to produce nanocarbons from bulk precursors.¹⁸ Prior to any re-aggregation *in situ* generated graphene is then subjected to functionalization. The unreacted, thus, unreactive sp²-carbons react mainly with “hot” reagents, namely radicals,¹⁹ fluorine,²⁰ diazonium salts,²¹ and nitrenes.²² Lower reactivity but better reaction control is achieved by cycloaddition reactions based on azomethine ylides²³ or benzyne.²⁴ Edge functionalization is already successful when conducting mild Friedel-Crafts acylation routines.²⁵

Nevertheless, all of the covalent approaches to graphene functionalization share the rehybridization of sp² carbon atoms in common. The resulting sp³ carbon atoms induce alterations in the electronic structure of graphene, as the crystal symmetry is broken around the point defect. In summary, introducing covalently-linked functionalities offers a great opportunity to gain control over the local electronic structure.

An alternative approach to stabilize graphene sheets in solution is ultrasonic treatment in organic solvents. Polar solvents such as NMP or GBL, which match the surface energy of graphene, turned out to be highly efficient for stabilizing few layer graphene

sheets in solution, preventing their re-aggregation into graphite, and providing a unique basis for further processing.²⁶

To overcome such intrinsic instability, graphene sheets were suspended in aqueous media with the help of amphiphilic surfactants—a process that is governed by hydrophobic effects.²⁷ Such integration opens novel routes to hybrid materials that exhibit even more exciting features than graphene itself. A leading example is the control over the doping level to adjust conductivity and charge carrier type transport. Such features are crucial for harvesting the full potential of graphene in transparent conductive electrodes, etc.²⁸ The most promising approaches evolve by combining the exfoliation and functionalization step with graphite as starting material. To surmount the strong van der Waals interactions that prevail between single graphene layers in the graphite crystal, amphiphilic molecules should strongly attach to the two dimensional sheets. This avoids stacking and / or re-aggregation while providing energy for exfoliation. As a matter of fact, electron deficient π -systems such as TCNQ were used in solution processes²⁹ to *n*-dope graphene sheets.³⁰

Importantly, the use of amphiphilic π -systems increases the driving force and renders the exfoliation process more dominant in terms of monolayer graphene, as next to π - π stacking also hydrophobic interactions are at force. A particularly successful amphiphile is pyrene carboxylic acids.³¹ Expanding the π -aromatic structure from pyrenes to perylenes further strengthens the stacking, which, in turn, is seen to increase the monolayer graphene distribution. In dendrimer-functionalized perylene derivatives a synergy of increased π -surface and amplified hydrophobic interactions ensure solubility and provide stability of the dispersions due to increased coulomb repulsions. Different starting materials—natural graphite or turbostratic graphite—as well as different solvents—water and NMP—were tested and electronic communication between the chromophore and graphene was unambiguously corroborated.³² Further efforts in this field have led to the realization of graphene flakes by means of processing of THF solutions of a ZnPc oligomer. The oligomer backbone is beneficial not only with respect to function

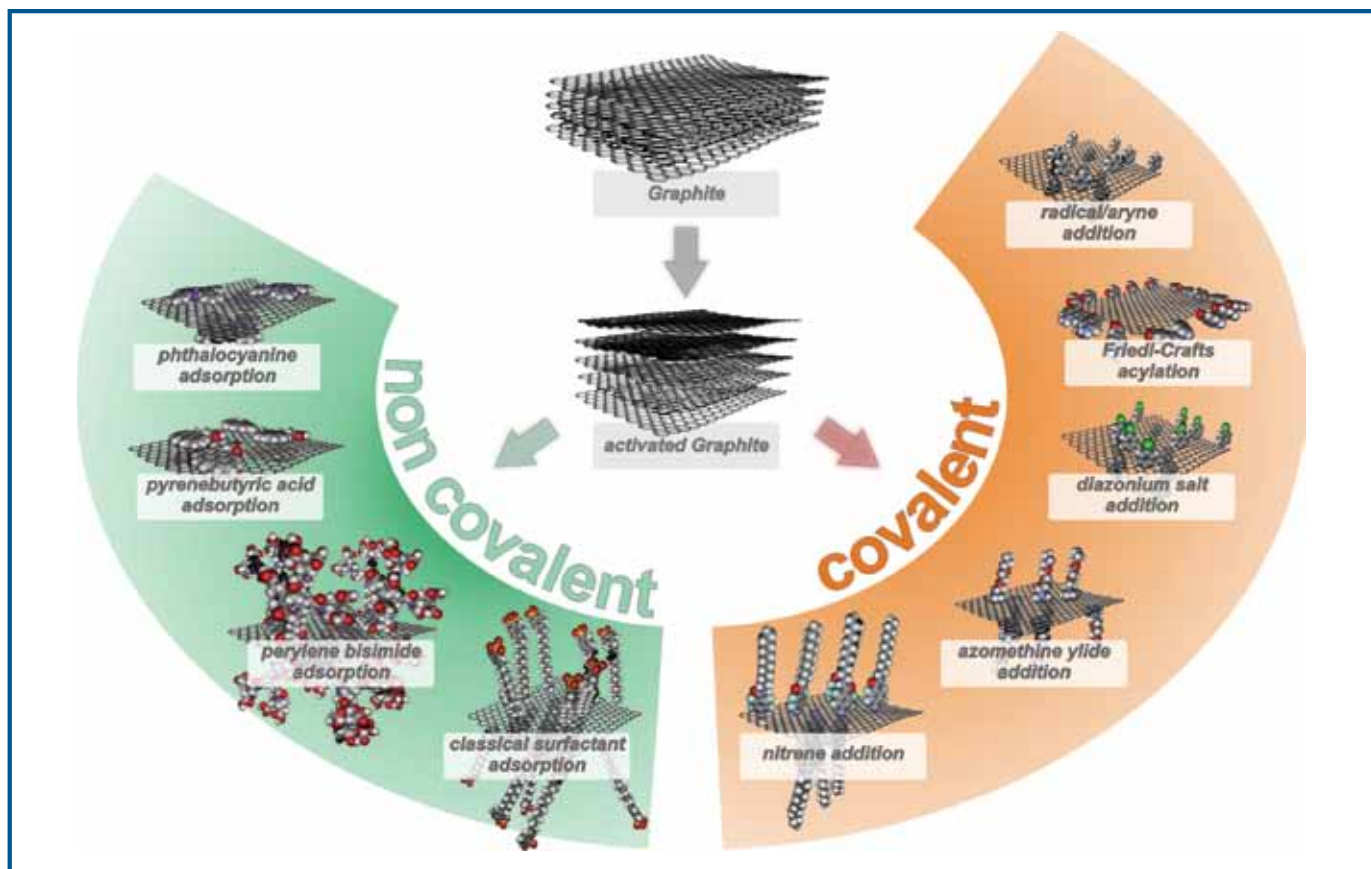


FIG. 2. Selection of currently available non-covalent and covalent functionalized graphenes.

as a template for several ZnPc but also to increase the overall π - π stacking with graphene. Strong electronic coupling between the individual components prevails and gives rise to new fingerprint absorptions and a nearly quantitatively electron transfer results in quenching of the ZnPc fluorescence.³³

Concluding Remarks

In summary, a variety of sophisticated approaches have been established to obtain stable dispersions of graphene. Differing between top down and bottom up approach, few preparations are known for the latter, while for the former starting from graphite a myriad of techniques are at hands. To overcome, however, the π - π stacking energy between individual graphene layers in graphite crystals an activation step needs to be implemented. Damaging the crystal lattice planes with harsh oxidants is certainly a viable option as it is routinely carried out during the synthesis of graphite oxide. The attached oxygen functionalities are inception to repulsive forces and flaking of individual layers takes place when subjected into protic media. Likewise, the use of alkali metal intercalations activates graphite without introducing sp^3 crystal defects. Here, charge transfer from the donating metals results in a product with widened interlayer distances. Nevertheless, non-covalent and covalent functionalization of the aforementioned starting materials are limited by the aggressive conditions necessary to post-process GO or GICs to get graphene, respectively. Functionalization is certainly a crucial step not only for stabilizing the graphene sheets, but also for harvesting the material's full potential by tuning electron-donor and electron-acceptor systems in solution-based processes. To this end, mild functionalization and exfoliation techniques are required, which would leave the lattice structure and the electronic properties of graphene intact. ■

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Dirk M. Guldi is one of the world-leading scientists in the field of charge transfer/nanocarbons. In particular, he is well-known for his outstanding contributions to the areas of charge-separation in donor-acceptor materials and construction of nanostructured thin films for solar energy conversion. His scientific career began at the University of Köln, from where he graduated in chemistry (1988) and from where he received his PhD (1990). After a postdoctoral stay at the National Institute of Standards and Technology in Gaithersburg/USA (1991/1992), he took a position at the Hahn-Meitner-Institute Berlin (1992-1994). Following a brief stay as a Feodor-Lynen Fellow at Syracuse University/USA he joined the faculty of the Notre Dame Radiation Laboratory/USA (1995). Then, after nearly a decade in the USA, the University of Erlangen-Nürnberg succeeded in attracting Dirk M. Guldi back to Germany. He is the recipient of numerous honors and awards: VCI Abschlussstipendium (VCI, 1990), Heisenberg Preis (DFG, 1999), Grammaticakis-Neumann Prize (Swiss Society of Photochemistry, 2000), JSPS Award (Japan Society for the Promotion of Science, 2003), JPP Award (Society of Porphyrins & Phthalocyanines, 2004), and Elhuyar-Goldschmidt Award (Spanish Chemical Society, 2009). He was elected chairman of the ECS Fullerenes, Nanotubes, and Carbon Nanostructures Division in 2008. He may be reached at dirk.guldi@chemie.uni-erlangen.de.

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