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 cyclododehydreative 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/functionization, 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 a strong acid—e.g., hydrazine i.e., alkali metals)—i.e., 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., carboxyls, 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/functionization, 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
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.

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. Prior to any re-aggregation in situ generated graphene is then subjected to functionalization. The unbent and, thus, unreactive sp²-carbons react mainly with “hot” reagents, namely radicals, fluorine, diazonium salts, and nitrenes. Lower reactivity but better reaction control is achieved by cyclo-addition reactions based on azomethine ylides or benzene. Edge functionalization is already successful when conducting mild Friedel-Crafts acylation routines. 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.

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. Such integration opens novel routes to hybrid materials that exhibit even more exiting 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. 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 processes to ndope graphene sheets. 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. 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. 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

![Image](image-url)
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 sp³ 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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