

# A Supramolecular Strategy to Leverage the Liquid-Phase Exfoliation of Graphite into Graphene: Inks and Light-Responsive Hybrid Materials

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Achieving the full control over the production as well as processability of high-quality graphene represents a major challenge with potential interest for numerous applications in opto-electronics, energy, sensing and composites. The outstanding effort dedicated to tackle this challenge in the last decade revealed that certain organic molecules are capable of leveraging the exfoliation of graphite with different efficiencies [1].

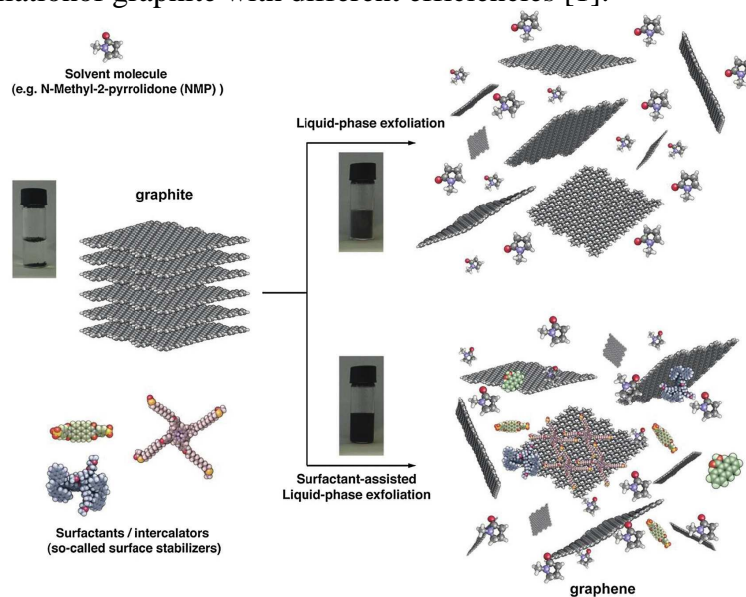


Figure 1: Schematic representation of the liquid-phase exfoliation process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules.

Self-assembly of molecular building blocks at the solid/liquid interface relies on a subtle interplay between molecule/molecule, molecule/substrate, molecule/solvent, and solvent/substrate interactions leading to the targeted 2D nanopatterns [2]. The use of small organic molecules such as dispersion-stabilizing agents is expected to promote the exfoliation of graphite when the chosen molecules have a strong affinity for the basal graphitic planes, being stronger than that of the solvent molecules interacting with graphene. A good starting point can be the use of alkanes, which are known to exhibit a high affinity for the surface of graphite/graphene [2].

In this framework, we have demonstrated that by mastering a supramolecular approach it is possible to improve the yield of graphene in liquid-phase exfoliation (LPE) process and produce high-quality graphene flakes from bulk graphite [3]. By using a molecular module possessing high affinity for the graphite surface, high concentration of graphene dispersions can be obtained. In particular, by using phenyloctane or arachidic acid molecules the amount of monolayer graphene increases by 10% and graphene concentration increases even by 50%. The LPE processed graphene dispersion was shown to be stable conductive ink. Moreover, recently we have also demonstrated that it is possible to correlate thermodynamics of molecular physisorption with the yield of LPE of graphene [4]. To attain a fundamental understanding on supramolecular approach for producing graphene dispersions in different organic solvents, we have carried out a comparative study by using fatty acids with increasing

the length of the aliphatic chain. Careful analysis revealed a significant increase in the yield of exfoliation with the length of the aliphatic chain. Furthermore, a remarkable increase of single-layer graphene flakes was observed in some cases. Our analysis shows that the shorter the aliphatic chain, the larger the entropic cost of forming a 2D self-assembled monolayer will be. These results suggest that our model could be used to predict the efficiency of supramolecular building blocks as graphene dispersion-stabilizing agents and eventually guide the chemical design of the next generation of exfoliators.

Multifunctional materials can be engineered by combining multiple chemical components each one conferring a well-defined function to the ensemble. We will show that the large conformational change associated with the *trans-cis* photochemical isomerization of alkyl-substituted azobenzenes can be used to harness the sonication-assisted exfoliation of graphite into graphene in solutions of such photochromic molecules acting as dispersion-stabilizing compounds [5]. We will demonstrate reversible photo-modulated current properties in two-terminal devices based on graphene-azobenzene nanocomposites associated to intercalation of the azobenzenes between adjacent graphene layers and the resulting increase in the interlayer distance when (photo)switching from the linear *trans*-form to the bulky *cis*-form of the photochromes. Our approach may open perspectives towards the development of new optically controlled memories for light-assisted programming and high-sensitive photosensors [6].

## References

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