Direct Liquid-Phase Exfoliation of Graphite via Diels-Alder reaction

Hugo Barès, Sébastien Bonhommeau, Jean-Baptiste Verlhac, Dario Bassani

Institut des Sciences Moléculaires, CNRS UMR 5255 – Université de Bordeaux, 351, Cours de la Libération, 33405 Talence, France
hugo.bares@u-bordeaux.fr

Since the discovery of the electronic properties of graphene in 2004,[1] many techniques to produce graphene films have been developed. The most common methods are Chemical Vapor Deposition (CVD)[2,3] and through micromechanical[1] or chemical[4] exfoliation of graphite. The latter are very cost effective and suitable for large-area device fabrication but generate defects and residual stress in the material that is deleterious to its performance. In particular, liquid-phase exfoliation of graphite requires the use of surfactants, or non-volatile and/or halogenated solvents that are impractical to remove following deposition. Likewise, chemical reduction of water-soluble graphite oxide does not lead to materials with the same electrical properties of pristine graphene due to the presence of residual defects.

We developed a process for the chemically-assisted exfoliation of graphite based on a reversible cycloaddition reaction.[5] This approach is highly efficient even in volatile organic solvents that are otherwise ineffective for exfoliation of graphite. The method relies on the Diels –Alder reaction between graphite and reactive dienes assisted by mild sonication. The formation of a “butterfly” adduct in which two sp^3 centers are present on the graphene skeleton is used to separate and solubilize functionalized graphene sheets. Because the Diels-Alder reaction is fully reversible, and that the adducts cannot migrate, gentle heating is sufficient to return the chemically modified graphene to its pristine state.

Thermogravimetric analyses, TEM, and confocal Raman spectroscopy were used to investigate the transformation and its consequences on the physical and electronic properties of graphene.

References

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