Direct and Defect-Free Liquid-Phase Exfoliation of Graphite
Assisted by a Reversible Cycloaddition Reaction

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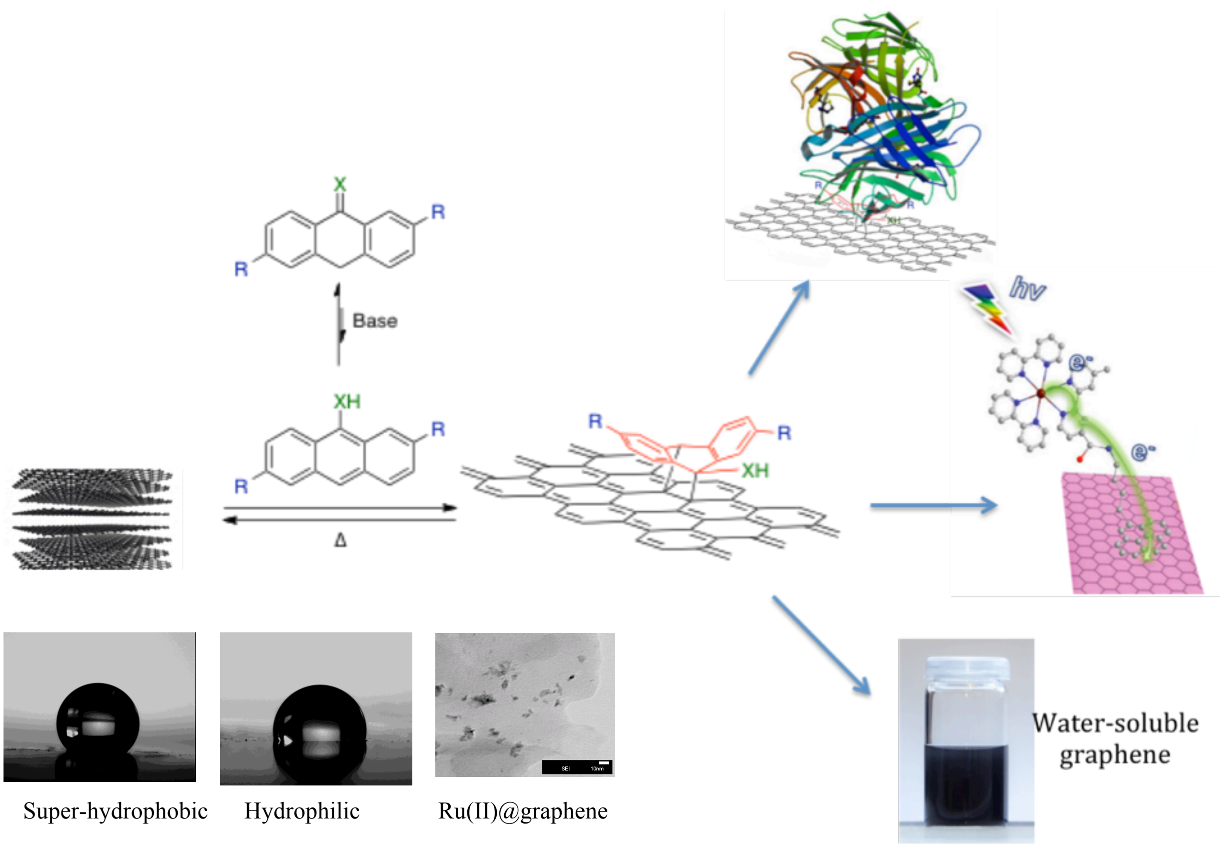
Since the discovery of the exciting properties of graphene, many techniques to produce and chemically modify graphene have been developed in order to expand and improve its properties in view of future applications. So far, covalent modification of graphene has been limited to oxidation, addition of free radicals, nitrenes, benzyne, and 1,3-dipolar cycloaddition of azomethine ylides. These processes are irreversible and, with the exception of oxidation, do not allow to obtain graphene from graphite.

We recently developed a novel route for the chemically-assisted exfoliation of graphite based on a reversible cycloaddition reaction.[1] It relies on the Diels-Alder reaction between graphite and a highly reactive masked diene using mild sonication. It is effective even in solvents that are otherwise ineffective for exfoliation of graphite, ranging from non-polar (toluene) to polar (acetonitrile, alcohols). By appropriate modification of the anthrone moiety, it is even possible to attain concentrations of 150 mg/L of graphene in water / isopropanol (1 : 1) mixtures and to control the wettability of the graphene films.

There is considerable interest in using functionalization to produce graphene solutions that do not aggregate, and this covalent Diels-Alder approach is a sustainable alternative because of the clean reversibility of the reaction. Indeed, the chemically exfoliated graphene returns to its pristine form under heating as confirmed by TEM and confocal Raman spectroscopy.

Furthermore, it is possible to introduce functional groups on the diene, thereby enabling post-functionalization of graphene sheets using different reagents. Thanks to this, a wide diversity of applications can be developed, ranging from enzyme immobilization to energy transfer (photodetection), and including recyclable catalysis. We will present the tuning of the surface properties of graphene, as well as its post-functionalization using, for example, a ruthenium (II)-based catalyst.



[1] D. Bassani, J.-B. Verlhac, H. Barès, Patent WO2015015120 (A3), 2015.