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Covalent Functionalisation of rGO and Nanodiamonds: Complementary Versatility and Applicability of Azomethine Ylide, Nitrile Oxide and Nitrone

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The existing synthetic protocols for the direct functionalization of carbon-based nanomaterials often entail limitations due to their harsh reaction conditions, which require the use of high temperatures for extended periods. This study aims to overcome these limitations by developing mild and efficient synthetic protocols around 1,3-dipolar cycloaddition. Beginning with the well-established azomethine ylide derivatization, we progress to the utilization of nitrile oxide, and of nitrone derivatives for the functionalization of reduced graphene oxide (rGO) as well as of nanodiamonds (NDs). This comparative work employs both classical heating and microwave activation with the aim of reducing reaction times and enhancing efficacy. Results demonstrate that nitrone can react at 60 °C and that the reaction temperature may be decreased to 30 °C with nitrile oxide. Excellent progress was made in reducing the large excess of dipoles typically required for derivatization. Nitrile oxide was proved to be the most efficient in terms of derivatization degree, while nitrone was the most versatile reagent, facilitating the decoration of the carbon nanolayer with disubstituted dihydroisoxazole. To accurately assess the degree of functionalization, the reaction products underwent characterization using various spectroscopic and analytical techniques. Additionally, an indirect evaluation of the reaction outcome was conducted through Fmoc deprotection and quantification.

Introduction

Carbon-based nanomaterials have been intensively investigated over the past two decades, and their production is now highly dedicated to technological applications.[1] Biomedical applications, hydrogen storage, contaminant sequestration, electrocatalysis, fuel and solar cells, batteries, electromagnetic shields, conductive paints and reinforcement for polymers are just some of the wide range of studied applications.[2] Carbon nanomaterials are classified based on their allotropic structure and hybridization (sp^3, sp^2, sp), leading to diverse forms like diamond, graphite, and carbyne.[3]

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Graphene offers distinct advantages, from an engineering standpoint, compared to CNT and fullerenes; its production yields a higher quality material with greater batch consistency, thus attracting stronger interest from industry. Great efforts have been made to improve the processability of graphene-based materials as low solubility, poor reactivity and limited accessibility have to be overcome before any chemical derivatization is possible.[4] Chemical exfoliation strategies, involving sequential oxidation and graphite reduction, yield a class of materials known as reduced graphene oxides (rGOs), which possess graphene-like characteristics.[5] rGO is a system characterized by graphene domains, defects and residual oxygen-containing groups on the surface of the sheets. It is dispersible in polar organic solvents, and thus potentially functionalized, thanks to enhanced reactivity stemming from the presence of defects associated with dangling bonds on the graphene lattice.[6]

NDs are composed of an sp^3 carbon structure surrounded by a shell consisting of functional groups. They exhibit a variety of sizes, shapes and surface chemistry that can be modulated by varying the synthetic approach.[7] ND-surface functional groups determine the chemical state of the carbon material, while their modification tunes both macroscopic and microscopic properties. Due to their non-toxic nature, these compounds have been extensively investigated for potential biomedical applications.[8]

Due to their high surface-to-volume ratio, the surface properties of NDs play an important role, and a range of different strategies have been pursued to grant the homogeneous and reactive distribution of surface species.[9]