

Identifying Reactive Sites on Graphene Sheets against 1,3-Dipolar Cycloaddition and Amidation Reactions

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The production of graphene by micromechanical cleavage¹ has triggered an enormous experimental activity. Since then, many studies have demonstrated that graphene monolayers possess novel structural,² electrical³ and mechanical⁴ properties. However many important issues need to be addressed before this material can be used in an ideal way. Much work has been produced that proposes chemical functionalization as a tool for tuning graphene chemical and physical properties. For example, chemical functionalization can render graphene dispersible in different solvents.⁵ To exploit the high mobility of graphene, the band gap engineering and controllable doping of semimetal graphene can be achieved by chemical functionalization.⁶ Moreover, the non-uniformity of graphene edges and the potential for dangling bonds are thought to have significant influence on their chemical properties and reactivity.⁷ Chemical modification of various forms of graphene, including reduced graphene oxide,⁸ liquid-phase exfoliated graphite,⁹ pristine graphene and its multilayers has been obtained.⁵ For instance, the aryl diazonium-based reaction has been extensively studied as a specific radical reaction on graphene layers.¹⁰ In graphene, the edges exhibit a higher reactivity than the interior during this specific reaction. Instead, we have recently reported the functionalization of graphene layers by condensation of a protected α -amino acid and paraformaldehyde,¹¹ demonstrating that even if the reactivity of graphene differs from that of fullerenes and carbon nanotubes, the 1,3-dipolar cycloaddition can be efficiently performed and yields a highly functionalized material taking place not just at the edges but also at the C=C bonds in the center of graphene sheets. However, further work needs to be performed for understanding the chemical structure of the functionalized graphene and their reaction mechanisms.

In this work we present a detailed study on the reactivity of graphene sheets stabilized in DMF using two different reactions: the 1,3-dipolar cycloaddition reaction and the amide-bond condensation reaction achieved between the free carboxylic groups already present in the exfoliated graphene and the amino functionalities of the attached moieties. Thus, we have functionalized graphene with a first generation polyamidoamine (PAMAM) dendron possessing an anchoring amine point and two terminal Boc-protected amines. Indeed, dendrimers and dendrons containing polar groups in their structures have been widely conjugated to carbon nanostructures in order to increase the solubility, modifying in this way their inherent apolar character to obtain more tunable structures.¹² Even more, the presence of free terminal amino groups can serve as ligands in the stabilization of gold nanostructures.¹³ As first step to identify the reactive sites on graphene layers the free amino groups were quantified by the Kaiser test. These amino groups selectively bind to gold nanoparticles, which can then be employed as contrast markers. The interaction between Au nanoparticles and functionalized graphene was followed by UV-Vis spectroscopy, while the morphological changes were characterized by transmission electron microscopy (TEM). The presence of the organic groups and their interaction with Au nanoparticles were verified by X-ray photoelectron spectroscopy. Au nanoparticles distributed uniformly all over the graphene surface were found for functionalized graphene via 1,3-dipolar cycloaddition. Instead, in functionalized graphene by amidation reaction Au nanoparticles were observed mainly at the edges of graphene sheets. All these results confirm that graphene produced by mild sonication of graphite in DMF are relatively free of defects and can be efficiently functionalized by well establish organic reactions.

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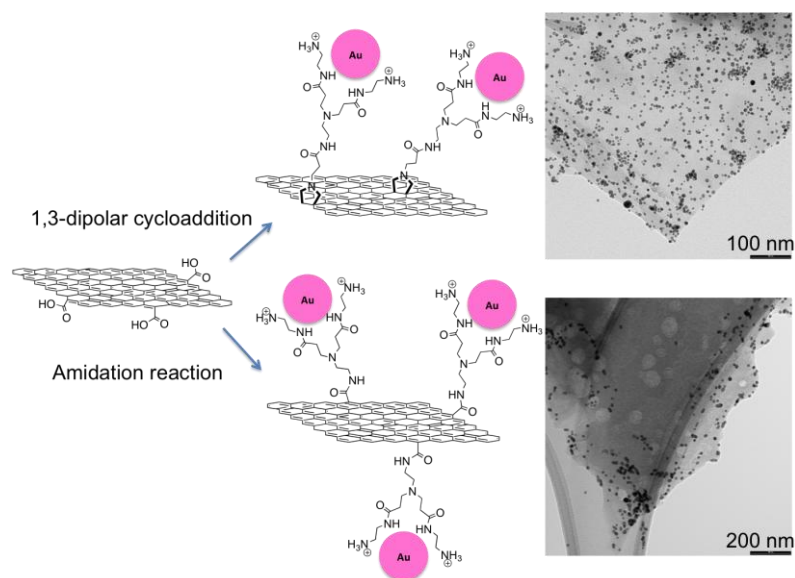


Figure 1: Schematic representation of functionalized graphene (left). TEM images of reactive sites on graphene marked by Au nanoparticles.