Chemistry on graphene oxide: how to control functionalization and biodegradation?

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Recent years have witnessed extensive research interest on graphene oxide (GO) and its great potential for applications in different fields including energy conversion and storage, electrochemical sensing, and cancer therapy. GO is constituted of a high number of oxygen-containing functions such as epoxides and hydroxyl groups on the basal plane of the GO sheet and, to a much lower extent, carboxylic acids and other carbonyl groups at the edges. These oxygenated moieties provide reactive sites for further derivatization of GO, allowing extension of its use to different applications. The large surface area and the chemical structure of GO enable several chemical modifications, making it an excellent platform for multifunctionalization through covalent and/or non-covalent approaches. Nevertheless, the high chemical reactivity of the oxygenated groups makes functionalization difficult to control as different reactions can occur concomitantly leading to side reactions. Besides monofunctionalization of GO,[1,2] covalent double functionalization allows better control of the specific attachment of either distinct molecules or nanoparticles through different reactions. In addition, the bond between GO and the new functional groups is more stable compared to non-covalent conjugates, a generally preferred approach. Until now, only few covalent double functionalization strategies of GO have been reported. Even if GO is composed of different oxygenated groups, most approaches exploited the same functional groups on the surface of GO or different functional groups without any selectivity.

In this context, we have extended the possibilities of double functionalization of GO through selective derivatization of the epoxides and hydroxyls. For this purpose, we have designed a strategy combining a nucleophilic epoxide opening reaction by an amine derivative with the derivatization of the hydroxyl groups by esterification or etherification.[3] We have also developed a simple and versatile strategy based on the combination of epoxide opening by a thiol derivative and a Michael addition of the hydroxyls with benzoquinone.[4] We used mild conditions to preserve the structure and properties of GO. Indeed, harsh conditions such as heating or the use of strong bases often cause partial reduction of GO, thus drastically decreasing its water dispersibility. Our strategies could be exploited to prepare multifunctional GO conjugates with potential applications in many fields ranging from materials science to biomedicine.

Biodegradation of graphene-based materials is an emerging issue due to their estimated widespread use in different industries. We have shown how specific functionalities on GO can help to increase its biodegradability by a peroxidase. GO functionalized with two substrates of the enzyme (coumarin or catechol moieties) displayed a faster and more efficient biodegradation over unmodified GO, strengthening its potential for biomedical applications.[5]

References

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