

Graphene oxide related forms for biosensing applications

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Abstract

Since the discovery of graphene in the last years¹ and with the great progress made in nanoscience and nanotechnology, its integration with biomolecules has received increased attention due to its physical, optical and chemical properties which are not available in other materials, such as its interesting molecular structure, high surface area and high conductivity capacity that improves the electron transfer². Since then, many graphene materials such as graphene oxide^{3,4}, graphene quantum dots⁵ or graphene nanoribbons have been reported⁶.

Graphene oxide with different oxidized grades, exhibits different defects levels due to the distribution of the oxygen atoms all over the graphene surface. Epoxy and hydroxyl groups lie above and below each graphene layer and the carboxylic groups are mostly located at the edges⁷. The presence of the oxygen groups onto the surface of the graphene sheet results in a highly hydrophilic character, which strongly affects the density of electronic states (DOS) and consequently the chemical reactivity and conductivity tuning its properties either to insulator or semimetallic⁸. The presence of epoxy and hydroxyl groups (within holes or not) in the basal plane and the flexibility of the oxidized graphene sheet can determine the preferential binding of enzymes. Instead, the edges which result to be hydrophobic interactuators reduce the capability for binding sites⁹.

The versatility of oxidative grades of graphene leads to transitions from insulator to semimetallic mainly after reducing processes¹⁰. Reduction modes such as reduction using hydrazine and thermal annealing¹¹ or bacterial treatment¹² which resulted in highly reasonable methods for the reconstruction of the graphene oxide sheet have been developed. The reduction of graphene oxide removes the oxygen groups and rehybridize the sp^3 carbon atoms to sp^2 carbon atoms¹³.

According to their properties, the graphene oxide opens the door for biofunctionalization with enzymes, DNA, antibodies, between other biomolecules. Therefore, due to the biofunctionalization capabilities combined with interesting electrochemical² and optical properties¹⁴ graphene oxide has greatly stimulated research interest for applications in (bio)sensing systems. The use of graphene-based

biosystems improves the detection levels¹⁵, being a great promise for routine sensitive, selective, rapid, and cost-effective analysis making them suitable for environmental, food safety and security and medical applications.

This work presents a detailed characterization of oxidized graphene oxide (oGO) and reduced graphene oxide (rGO) sheets on screen-printing electrodes, one of the most interesting platforms for electrochemical biosensors. The electrochemical response is sensitively followed by using catechol as a proof of concept analyte. For this study we have used highly oxidized graphene oxide (oGO) which have been reduced afterwards with hydrazine⁴ for de-oxygenation of oGO. The electrochemical responses of this reduced graphene oxide (rGO) have been compared with the responses obtained for oGO and their performance has been accordingly discussed with various evidences obtained by optical techniques.

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Figure

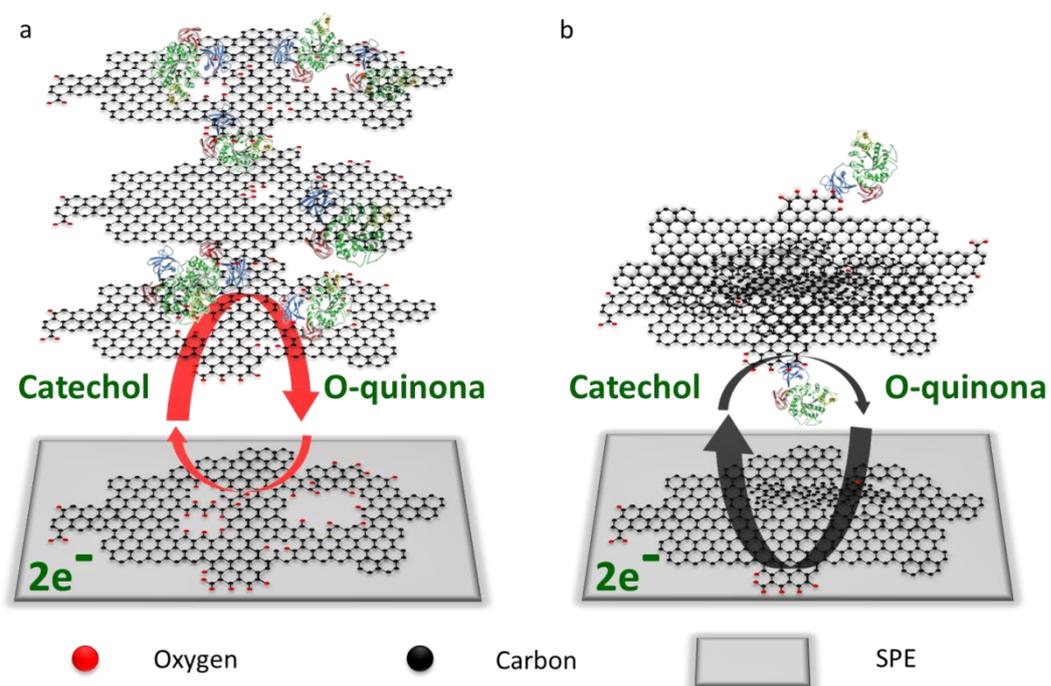


Figure 1. Schematic diagram (not in scale) displaying the enzyme (Tyrosinase) and reactions involved in the catechol detection at the SPE modified with oGO (a) and rGO (b).