Biosensors and Bioelectronics 52 (2014) 281–287

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Structure effect on graphene-modified enzyme electrode glucose sensors

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ARTICLE INFO

Article history:
Received 3 May 2013
Received in revised form
28 June 2013
Accepted 10 July 2013
Available online 2 August 2013

Keywords:
Graphene
Glucose
Biosensor
Enzyme electrode

ABSTRACT

Using structural characterizations and electrochemical measurements, we explored and investigated the effect of the structure of enzyme electrodes with glucose oxidase (GOD) that were modified by reduced graphene oxide (rGO) sheets . The rGO sheets with different defect density, layers, and oxygen concentrations were chosen to modify the enzyme electrode, and all the modified enzyme electrodes exhibited excellent electrocatalytic activities and performances towards glucose. The abundant defects in rGO induce easy absorption of GOD. At a low oxygen concentration, rGO sheets help to induce the direct electron transfer (DET) on the rGO-modified electrode, and at a higher oxygen concentration, the reduction of H_2O_2 occurred instead of DET on the surface of the rGO-modified electrode. When rGO modified the enzyme electrode under the working model of H_2O_2 reduction, an increase in the number of the oxygen functional groups could lead to an increase in the absorption of GOD, resulting in the improvement of the affinity and sensitivity of the biosensor. The rGO-modified enzyme electrode can provide faster response, higher sensitivity, and better affinity by optimizing and controlling the structure of graphene and its derivatives.

1. Introduction

Since Clark and Lyons (1962) proposed the concept of glucose enzyme electrodes in 1962, people have developed three generations of glucose biosensors: the first generation was based on monitoring the reduction of hydrogen peroxide, the second generation used as an inserted electron transfer mediator, and the third generation was based on detecting direct electron transfer (DET) (Wang, 2001) (Shan et al., 2009). In fifty years of research and exploration, glucose biosensors based on the glucose oxidase (GOD) electrode have been widely studied and used in clinical detection of diabetes, biological analysis, environmental monitoring, and in applications in the food processing industry (Wang, 2001). Currently, with the development of nanoscience and nanotechnology (Du et al., 2011), the study of enzyme electrode biosensors modified with nanomaterials and nanostructures has received broad attention, due to the possibility of using the various properties of nanomaterials with excellent electric properties, high surface area, and ease of functionalization (Ma et al., 2012; Wang et al., 2011b). The modification of an enzyme electrode through nanomaterials and nanostructures, such as silicon nanowires (Elfström et al., 2008), ZnO nanostructures (Lei et al., 2010; Lei et al., 2011), and carbon nanotubes (Bai et al., 2012), is a highlight of the fields of nanoscience and bioelectronics.

Graphene, a two-dimensional (2D) honeycomb lattice of carbon atoms that was isolated as a single layer in 2004 (Novoselov et al., 2004), has captured remarkable attention due to its excellent physical and chemical properties, such as its large surface area (theoretically, 2630 m^2/g for single-layer graphene), excellent electrical conductivity, high thermal conductivity, strong mechanical strength, and good biocompatibility (Guo and Dong, 2011b). Among all of graphene's remarkable properties, high surface area, ease of functionalization, excellent electron transfer, and good biocompatibility make it appropriate for application in enzyme electrode biosensors (Guo and Dong, 2011a).

The study of the application of graphene and its derivatives to enzyme electrode biosensors began in 2009. Niu et al. (Shan et al., 2009) first demonstrated that graphene could be used as an enhanced material for the direct electrochemistry of GOD to construct glucose biosensors. Lin et al. (Wang et al., 2010) demonstrated that N-doped graphene displayed a higher electrocatalytic activity for the reduction of hydrogen peroxide and for the rapid direct electron transfer kinetics for GOD. Dai et al. (Liu et al., 2010) fabricated glucose biosensors through the covalent attachment between carboxyl acid groups on graphene oxide (GO) sheets and the amine of GOD, and Qiu et al. (Qiu et al., 2011) utilized a synergy effect of GO and chitosan to fabricate a glucose

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http://dx.doi.org/10.1016/j.bios.2013.07.022

biosensor. In summary, enzyme electrodes modified by graphene and its derivatives exhibited broad linearity, good sensitivity, stability and reproducibility. However, the reported effects of graphene and its derivative structures on the properties of the modified enzyme electrode are vague.

In this paper, we studied the relationship between the reduced graphene oxide (rGO) structure and the electrochemical properties of enzyme electrodes with GOD modified by rGO sheets. Three rGO sheets with different layers, defect densities, and oxygen contents were characterized using a field-emission scanning electron microscope (FESEM), a Raman scattering spectroscope, and an X-ray photoelectron spectroscope (XPS). The low oxygen concentration of the rGO sheets helps to induce direct electron transfer (DET) on the electrode; in contrast, a higher oxygen concentration no longer generates DET but rather reduces H_2O_2 on the surface of the electrode. Thus, increasing the oxygen

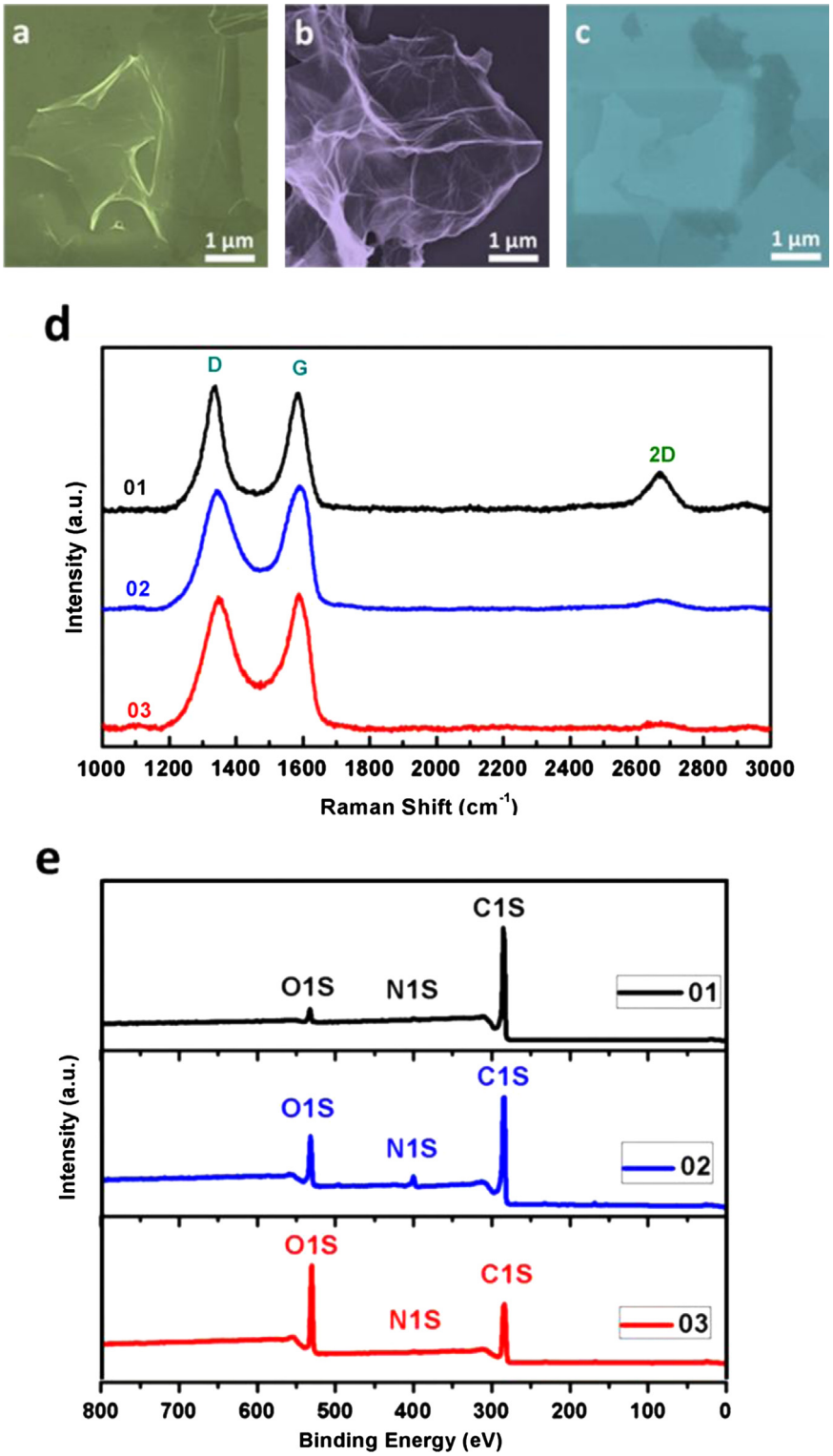

Fig. 1. Morphologies and structures of the rGO sheets. FESEM of the rGO sheets: (a) rGO01, (b) rGO02 and (c) rGO03; (d) Raman spectra and (e) the entire range of the XPS spectra.