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Review

Recent advances in electrochemical biosensing schemes using graphene and graphene-based nanocomposites

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ABSTRACT

The last decade has witnessed tremendous advances in the use of graphene and graphene-based nanocomposites for the fabrication of electrochemical (EC) sensors and biosensors with improved analytical performance. With unique and highly desirable morphology, chemical/thermal stability and EC properties, the graphene-based materials are paving way to the implementation of mediatorless EC detection schemes with direct electron transfer. This approach enables the development of highly performed biosensors with respect to detection sensitivity, precision, specificity, and stability. This review provides a comprehensive overview of the field apart from providing intensive information of the fabrication, properties, characterization and EC applications of graphene and its nanocomposites. Two key challenges, the lack of international regulatory guidelines for nanotoxicity analysis and potential mass production of analytical devices, will also be discussed along with the trends in nanobiotechnology and the requirements in healthcare and industrial applications.

Contents

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1. Introduction

Graphene becomes the most widely used nanomaterial of the 21st century for a plethora of diversified applications [1–6]; thanks to the pioneering work of Geim and Novoselov on this exciting material [7]. Graphene [8] exhibits a high specific surface area to accommodate very high biomolecule loadings to impart excellent detection sensitivity. Its high conductivity and a small band gap facilitate the conduction of electrons between the biomolecules and the graphene surface. Graphene with high purity and its derivatives are chemically inert and cost-effective with greater homogeneous surfaces than carbon nanotubes (CNTs).

There are significant advances in the synthesis of graphene and its applications in the last decade [9]. The top-down fabrication of graphene is based on graphite exfoliation by physical, electrochemical, and chemical procedures. Chemical vapor deposition (CVD) is one of the most prospective "bottom-up" methods for the mass production of graphene besides the chemical or thermal reduction of graphene oxide (GO). The commercially available graphene is known as graphene nanoplatelets (GNP), a crystalline or flake form of graphite with many graphene sheets stacked together (Fig. 1). However, single and bilayer graphene have also been developed [10]. Functional groups such as carboxyl, hydroxyl, sulfonate, acid chloride and amine are introduced [11–13] for subsequent bioconjugation. Several nanocomposites are easily prepared from graphene or its derivatives by modification with polymers, conducting polymers, surfactants, and other nanomaterials, e.g., quantum dots and metal nanoparticles [11,12]. These resulting nanocomposites often exhibit superior electrical conductivity, critically improved sensitivity, greater shelf-life, and less biofouling, compared to pristine graphene.

In biosensing applications, the direct electron transfer (DET) between a redox enzyme, e.g., glucose oxidase (GOx) and the underlying electrode surface has opened up the possibility for the fabrication of efficient and reagentless biosensors [3,13] with high selectivity. The graphene-functionalized electrodes exhibit superior analytical performance with negligible interference from biological substances and drug metabolites and excellent anti-fouling. The graphene-/graphene-based nanocomposite modified electrodes (G/GNE) have been advocated for biomarkers, proteins, DNA, heavy metals, inorganic and organic analytes of clinical, environmental and bioanalytical importance. Of significance is the widespread application of G/GNE for detecting blood glucose, which is inspired by a vast potential market of diabetic management at the consumer level. Apart from glucose, a large number of other analytes, such as neurotransmitters/neurochemicals, amino acids, disease biomarkers, proteins, DNA, cells, environmental contaminants, etc. have also been detected.

Considering an unprecedented number of publications related to graphene for the last two years alone (Fig. 2), this review aims to update the most recent developments of EC sensing/biosensing employing G/GNE using the literature information dated from 2012. The strategies employed for the fabrication of G/GNE are described followed by their properties and electrochemistry of graphene. Subsequently, the EC sensing applications of G/GNE for the detection of various

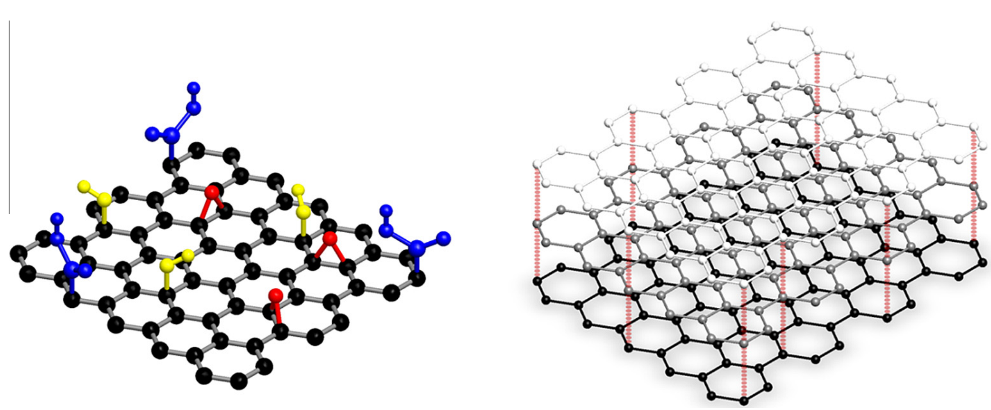

Fig. 1 – Single- (left) and multi-layered (right) graphene. The yellow, red and blue groups in single-layered graphene are hydroxyl, ether and carboxyl groups, respectively. Reproduced with permission from J. Nanomed. Nanotechnol. [14]. (A colour version of this figure can be viewed online.)