Chemosphere xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Chemosphere

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

Carbon nanomaterial-based electrochemical biosensors for label-free sensing of environmental pollutants

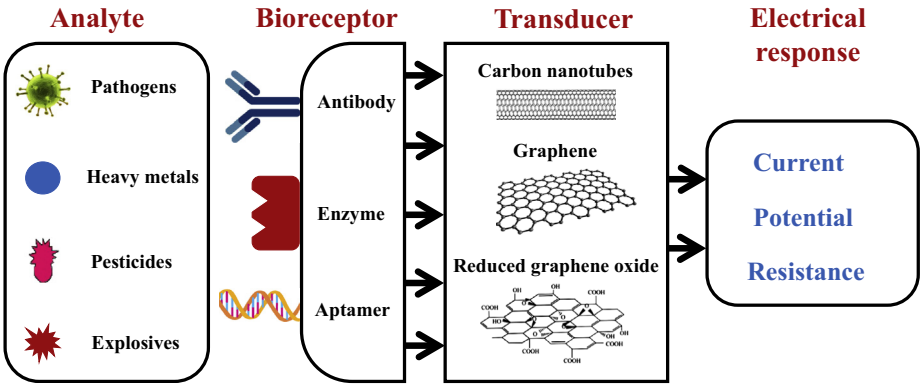
Pankaj Ramnani [a,1], Nuvia M. Saucedo [b,1], Ashok Mulchandani [a,*]

[a] Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, United States
[b] Department of Chemistry, University of California, Riverside, CA 92521, United States

HIGHLIGHTS

- Surface carbon atoms make carbon nanomaterials (CNM) superior as electrochemical sensor.
- Functionalizing with biorecognition elements impart CNM excellent selectivity.
- CNM-based electrochemical biosensors are excellent for environment monitoring.
- CNM-based electrochemical biosensors for low-cost, on-site pollutants detection discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 December 2014
Received in revised form 17 April 2015
Accepted 21 April 2015
Available online xxxx

Keywords:
Carbon nanotubes
Graphene
Electrochemistry
Pollutants
Aptamers
Antibodies

ABSTRACT

Carbon allotropes such as graphene and carbon nanotubes, have been incorporated in electrochemical biosensors for highly sensitive and selective detection of various analytes. The superior physical and electrical properties like high carrier mobility, ambipolar electric field effect, high surface area, flexibility and their compatibility with microfabrication techniques makes these carbon nanomaterials easy to integrate in field-effect transistor (FET)/chemiresistor type configuration which is suitable for portable and point-of-use/field-deployable sensors. This review covers the synthesis of carbon nanostructures (graphene and CNTs) and their integration into devices using various fabrication methods. Finally, we discuss the recent reports showing different sensing platforms that incorporate biomolecules like enzymes, antibodies and aptamers as recognition elements for fabrication of simple, low cost, compact biosensors that can be used for on-site, rapid environmental monitoring of environmental pollutants like pathogens, heavy metals, pesticides and explosives.

1. Introduction

With the rapid industrialization and urbanization over the past few decades, environmental issues like the pollution of air, water and other natural resources have been a major global concern. Some of the major anthropogenic sources that contribute toward the deterioration of environments are derived from industrial and agricultural activities such as improper solid waste disposal and bioaccumulation of toxic wastes, massive use of pesticides and synthetic fertilizers, and use of biological warfare agents. Humans are often exposed to a myriad of adverse health effects due to the toxicity of these pollutants, mainly through the

* Corresponding author.
E-mail address: adani@engr.ucr.edu (A. Mulchandani).
[1] Equal contributions.

http://dx.doi.org/10.1016/j.chemosphere.2015.04.063
0045-6535/

ingestion of contaminated food and drinking water, as well as the inhalation of ambient air with high concentrations of pollutants. These issues emphasize the importance of developing reliable, highly sensitive, user-friendly and cost effective tools for constant monitoring and detection of pollutants in different mediums.

In spite of recent advances in technology, using inexpensive yet reliable devices for the selective and accurate detection of pollutants in complex samples remains a challenge due to interfering species often found within the sample matrix. The most commonly used analytical techniques for detection include gas chromatography/mass spectrometry (GC/MS) (Auroux et al., 2002) and atomic absorption spectroscopy (AAS) (Van Loon, 2012). Though highly sensitive, these analytical techniques are time-consuming, expensive, require a lot of expertise to be operated and are not easy to be deployed in the field due to their bulky size. Overcoming these limitations, chemical sensors have emerged as an alternative, a simple, rapid, cost-effective and portable tool for analyzing environmental security threats. Biosensors, a class of chemical sensors, are self-contained integrated devices that are capable of providing specific qualitative or semi-quantitative analytical information by integrating a biorecognition element which is in direct spatial contact with a transduction element (Thévenot et al., 2001). The biorecognition element, usually an enzyme, antibody or an oligonucleotide selectivity binds a specific analyte from the given sample and the transducer element converts the chemical event into a measurable signal like current, mass, fluorescence or pH change. Among these different platforms, sensors based on a change in electrical property remain an attractive option due to their simple operation, facile fabrication process and device integration. They typically operate by measuring the change in conductivity of the sensor upon adsorption of the analyte molecule onto the sensory element.

2. Carbon-based nanomaterials

Over the past two decades, advancements in the field of nanotechnology toward synthesis of nanomaterials and understanding their fundamental properties have been substantial. Carbon-based nanostructures, including carbon nanotubes, graphene and graphene oxide, have been hot topics in the field of material science (Geim and Novoselov, 2007). Owing to their intriguing physical, chemical and electrical properties, carbon-based nanomaterials have thus emerged as potential candidates for development of next generation miniaturized biosensors (Wang, 2005; Shao et al., 2010; Zhou et al., 2009b). The planar geometry of graphene and tubular geometry of carbon nanotubes ensures exposure of almost all the surface atoms which enables binding a significant fraction of analyte molecules to the transduction material. The Debye length, λ_D, a measure of the field penetration into the bulk, is comparable to the dimensions of these nanostructures, which causes significant modulation of their electronic properties upon exposure to chemicals. These properties enable label-free detection of analytes with higher sensitivities and lower limits of detection. Furthermore, they can easily be configured as field-effect transistors (FETs) using lithography techniques and integrated with the modern microelectronics for fabrication of multiplexed devices that can detect a number of analytes simultaneously (Cullen et al., 1990). Apart from graphene and carbon nanotubes, other carbon-based nanomaterials, such as carbon nanofibres (CNFs) (Periyakaruppan et al., 2011; Adabi et al., 2015) and nanocrystalline diamond (NCD) (Härtl et al., 2004) also exhibit improved electrochemical activity. However, the number of reports exploring the use of these nanomaterials for electrochemical detection of environmental pollutants are limited. The scope of this review is to discuss the latest progress in the field of electrochemical biosensors based on graphene and carbon nanotubes for sensing of environmental pollutants such as pathogens, heavy metals, pesticides and small organic pollutants.

2.1. Graphene

2.1.1. Structure and properties

Graphene is a two-dimensional (2-D) sheet of sp^2 hybridized carbon atoms arranged in a honeycomb shaped lattice. As shown in Fig. 1(a), graphene is the basic building block of other carbon allotropes as it can be wrapped to get 0-D fullerenes, rolled up cylindrically to get pseudo 1-D carbon nanotubes and stacked to form 3-D graphite. (Geim and Novoselov, 2007) The two-dimensional geometry of graphene results in a very high surface area (theoretically calculated to be 2630 m^2/g, almost twice as that of SWCNTs), thus exposing a significant fraction of surface atoms to analytes. Graphene is a semiconductor with a zero band-gap. It exhibits ambipolar electric field effect with charge carrier mobilities exceeding 15,000–20,000 cm^2/Vs even at room temperature (Fig. 1(b)). This makes the electronic properties of graphene sensitive to both electron-donating and electron-withdrawing molecules. In addition, graphene exhibits superior mechanical and thermal properties, optical transparency (~97.7%) and flexibility. These physical, chemical and electrical properties make graphene an attractive candidate for the fabrication of label-free electrochemical biosensors with high sensitivity (Huang et al., 2011; Ohno et al., 2010).

2.1.2. Synthesis

2.1.2.1. Exfoliation. Graphene was first isolated in 2004 at the University of Manchester by Novoselov and Geim using scotch-tape exfoliation of highly oriented pyrolytic graphite (HOPG) (Novoselov et al., 2004). This method, also called micromechanical exfoliation or peel-off method, relies on isolation of individual π-stacked layers in graphite by repeated peeling using a scotch tape. Graphene obtained using this method is usually defect-free and of high quality, however, the sample size is very small (few microns) and suffers from poor yield. This method has been limited to lab-scale fundamental studies and not for commercial synthesis of graphene. To overcome these limitations, liquid-phase exfoliation of graphite in solvents like N-methyl-pyrrolidone (Hernandez et al., 2008) and surfactant (sodium dodecyl benzene sulfonate) solution has been demonstrated (Lotya et al., 2009). This technique, though facile, has its own limitations such as the resulting graphene film dimensions and the incomplete removal of solvents which tend to have high boiling points. Due to its low cost and low number of processing steps involved, this technique provides a potential route for large-scale synthesis of graphene-based sensors.

2.1.2.2. Reduced graphene oxide. Graphite oxide (GO) is synthesized by Hummers method which involves treatment with potassium permanganate ($KMnO_4$) and concentrated sulfuric acid (H_2SO_4) for simultaneous oxidation and exfoliation of graphite (Hummers and Offeman, 1958). The acid treatment introduces polar oxygen functional groups like epoxies, carbonyls, hydroxyls, etc. which makes GO hydrophilic. Using mild sonication, the GO sheets can be dispersed with ease in many solvents, particularly well in water (Paredes et al., 2008). Thereafter, the colloidal solution of graphene oxide can be reduced to graphene using different treatments like chemical reduction by directly adding reducing agents like hydrazine (Stankovich et al., 2007) or by thermal reduction using elevated temperatures (200–900 °C) (McAllister et al., 2007). Electrochemical reduction by immobilizing the GO onto an electrode surface and successively performing reducing scans by sweeping potential from 0 to −1.5 V is perhaps the simplest and

Please cite this article in press as: Ramnani, P., et al. Carbon nanomaterial-based electrochemical biosensors for label-free sensing of environmental pollutants. Chemosphere (2015), http://dx.doi.org/10.1016/j.chemosphere.2015.04.063