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Short Review

Synthesis and utilization of carbon nanotubes for fabrication of electrochemical biosensors

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ABSTRACT

This review summarizes the most recent contributions in the fabrication of carbon nanotubes-based electrochemical biosensors in recent years. It discusses the synthesis and application of carbon nanotubes to the assembly of carbon nanotube-based electrochemical sensors, its analytical performance and future expectations. An increasing number of reviews and publications involving carbon nanotubes sensors have been reported ever since the first design of carbon nanotube electrochemical biosensors. The large surface area and good electrical conductivity of carbon nanotubes allow them to act as "electron wire" between the redox center of an enzyme or protein and an electrode's surface, which make them very excellent material for the design of electrochemical biosensors. Carbon nanotubes promote the different rapid electron transfers that facilitate accurate and selective detection of cytochrome-c, β-nicotinamide adenine dinucleotide, hemoglobin and biomolecules, such as glucose, cholesterol, ascorbic acid, uric acid, dopamine pesticides, metals ions and hydrogen peroxide.

1. Introduction

Carbon nanotubes (CNTs) have become some of the most attractive nanomaterials in nanotechnology revolution. With the continuous progress of nanotechnology in material science, carbon nanomaterials have been given special attention because of their remarkable mechanical and electrical properties and are being used in many scientific and engineering research projects [1,2]. In recent years, CNTs have received great attention as promising carbon-based nanoelectronic devices. Because of their exceptional physical, chemical, and electrical properties, namely, a high surface-to-volume ratio, their enhanced electron transfer properties and their high thermal conductivity, CNTs can be employed effectively as electrochemical sensors. The integration of CNTs with a functional group provides a good and solid support for the immobilization of enzymes and has made CNTs to attract considerable attention in electroanalysis and biosensing.

CNTs are rolled up sheets of graphene. These can be single sheet cylinders giving single-walled carbon nanotubes (SWCNTs), or multiple concentric cylinders of increasing diameter about a common axis separated by 0.34 nm that are known as multi-walled carbon nanotubes (MWCNTs) [3]. There is also double wall carbon nanotube (DWCNT), but MWCNT have shown the most promising appearance to the market place in recent times (Fig. 1).

Recently, researchers have focused great attention on CNTs and their derivatives, and they are being studied in nearly every field of science [1], medicine [4–6] and engineering [7]. CNTs-based materials can have a profound impact on electronic and optoelectronic devices [8], chemical sensors [9,10], nanocomposites [11–19], optical biosensor [20,21] and energy storage [16,22]. New applications of CNT-nanomaterials in electrochemical sensors and biosensors are now on the increase with the advent of nanotechnology [23]. There are various CNT-nanomaterials [24–30], including carbon nanotube metal nanoparticle (NP) [31], nanocomposite [14,19], metal alloy NP [14], magnetic NP [32,33], nanowires [34–37], nanofibers [27,38] and nanorod [39]. CNTs have been used as electrical connectors between the electrodes and the redox centers of the biomolecules [40–44]. Sensors based on CNTs and graphene have shown excellent performance in electrochemical detection of metal ions, pesticides and other pollutants. The properties of CNTs, such as fast electron transportation, high thermal conductivity, excellent mechanical flexibility and good biocompatibility, make it a potential in the fabrication of sensitive electrochemical biosensor [45].

CNTs were discovered in 1991 by Iijima [46] and they have been the goal of numerous researchers due to their unique structural, electronic and mechanical properties that make them a very

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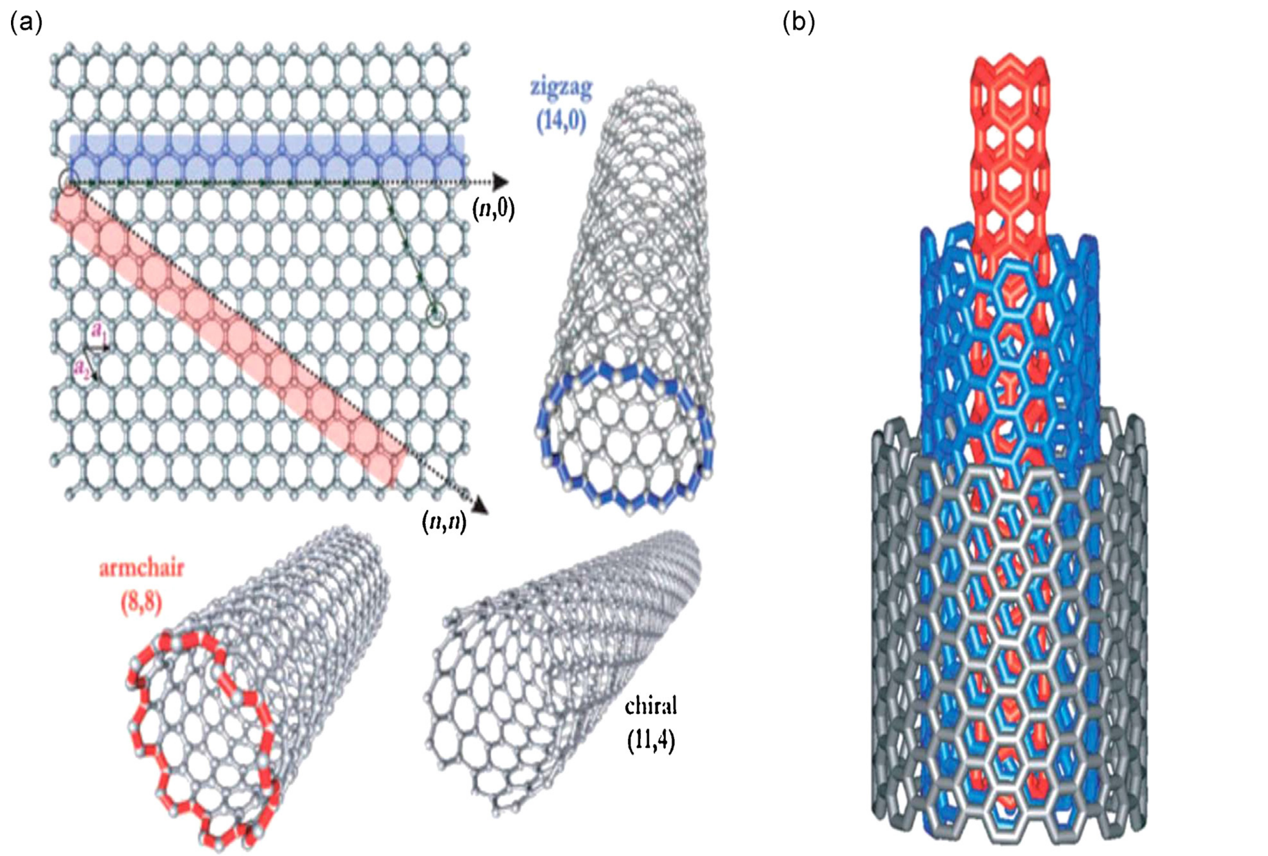

Fig. 1. (a) Roll-up of a graphene sheet leading to three different types of SWCNTs; (b) structure of a multi-walled carbon nanotube made up of three shells of differing chirality [76].

attractive material for a wide range of applications. Since their discovery in 1991, study of the properties and applications of CNTs has rapidly increased. The studies demonstrated that CNTs can significantly enhance the electrochemical reactivity of important biomolecules and can promote the direct electron-transfer reaction of proteins. Additionally, CNT-modified electrodes can also relieve the surface fouling effects. These properties make CNTs extremely attractive for a wide range of electrochemical biosensors. Their unique structure provides an exceptional electric-current-carrying capacity along their length (1000 times higher than copper wires) which leads to attractive CNT-based new electrode materials. CNTs excellent intrinsic properties, such as high surface area, unique physical properties, chemical stability and high electrical conductivity, lead to their wide potential applications in nanoelectronics, composite materials, energy research and biomedicine [5,14,47–56]. Nowadays, CNTs remarkable electronic, optical, mechanical, thermal and electrochemical properties have made them suitable electronic materials for electrochemical sensing, as CNTs have very good low-noise electronic [57]. Many groups all over the world are doing exciting works using CNTs and their hybrids in applications such as super capacitors [28,57–62], clinical chemistry [20,63], medicine [64], fuel cells [28,65–72], batteries [73–76], biodiesel [72], photocatalysis [77], photovoltaic [66,78], chemical and biosensors [10,76,79,80], greenhouse gas sensor [81], gas sensors [81–90], photonics [21], solar cell [57,69,73,78], light-emitting diodes (LEDs) [57], optical sensor [91], energy [92,93] optoelectronics, photocatalyst, biofuel [94], thin-film transistors and field effect transistor (FET) [1,20,57,95] (Fig. 2). In this review, the recent progress of electrochemical sensors based on functionalized CNTs will be discussed, covering synthesis, functionalization, nanocomposite electrochemical process and representative examples. It will be demonstrated that functionalized CNTs as templates, carriers, immobilizers and transducers are suitable innovations for the construction of sensitive electrochemical sensors (Fig. 3).

2. Synthesis of CNTs

A number of different routes to synthesize CNTs have been demonstrated over recent years. The three main synthesis techniques for CNTs production are arc discharge [57], laser ablation [96] and chemical vapour deposition (CVD) [57,97,98]. Dumitrescu et al. [99] named the techniques as electric arc discharge, laser ablation, high-pressure carbon monoxide (HiPCO) and catalyzed chemical vapour deposition (cCVD) [100]. Baskar et al. [101] named the techniques that have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, chemical vapor deposition, saline solution method and flame synthesis method. CNTs generally obtained by the arc method or hydrocarbon pyrolysis are multi-walled, having several graphitic sheets or layers [102].

Single-walled carbon nanohorns (SWCNHs) are horn-shaped single-walled tubules with a conical tip. They are generally synthesized by laser ablation of pure graphite without using metal catalyst with high production rate and high yield, and typically form radial aggregates. SWCNHs are essentially metal-free and very pure, which avoids cumbersome purification and makes them user-friendly and environmentally benign. Currently, SWCNHs have been widely studied for various applications, such as gas storage, adsorption, catalyst support, drug delivery system, magnetic resonance analysis, electrochemistry, biosensing application, photovoltaic and photo electrochemical cells, photodynamic therapy and fuel cells. Multi-walled (MWNTs), double-walled (DWNTs) and single-walled (SWNTs) carbon nanotubes