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Review on carbon-derived, solid-state, micro and nano sensors for electrochemical sensing applications

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ABSTRACT

The aim of this review is to summarize the most relevant contributions in the development of electrochemical sensors based on carbon materials in the recent years. There have been increasing numbers of reports on the first application of carbon derived materials for the preparation of an electrochemical sensor. These include carbon nanotubes, diamond like carbon films and diamond film-based sensors demonstrating that the particular structure of these carbon material and their unique properties make them a very attractive material for the design of electrochemical biosensors and gas sensors.

Carbon nanotubes (CNT) have become one of the most extensively studied nanostructures because of their unique properties. CNT can enhance the electrochemical reactivity of important biomolecules and can promote the electron-transfer reactions of proteins (including those where the redox center is embedded deep within the glycoprotein shell). In addition to enhanced electrochemical reactivity, CNT-modified electrodes have been shown useful to be coated with biomolecules (e.g., nucleic acids) and to alleviate surface fouling effects (such as those involved in the NADH oxidation process). The remarkable sensitivity of CNT conductivity with the surface adsorbates permits the use of CNT as highly sensitive nanoscale sensors. These properties make CNT extremely attractive for a wide range of electrochemical sensors ranging from amperometric enzyme electrodes to DNA hybridization biosensors. Recently, a CNT sensor based fast diagnosis method using non-treated blood assay has been developed for specific detection of hepatitis B virus (HBV) (human liver diseases, such as chronic hepatitis, cirrhosis, and hepatocellular carcinoma caused by hepatitis B virus). The linear detection limits for HBV plasma is in the range 0.5–3.0 μL^{-1} and for anti-HBVs 0.035–0.242 mg/mL in a 0.1 M $NH_4H_2PO_4$ electrolyte solution. These detection limits enables early detection of HBV infection in suspected serum samples. Therefore, non-treated blood serum can be directly applied for real-time sensitive detection in medical diagnosis as well as in direct *in vivo* monitoring.

Synthetic diamond has been recognized as an extremely attractive material for both (bio-) chemical sensing and as an interface to biological systems. Synthetic diamond have outstanding electrochemical properties, superior chemical inertness and biocompatibility. Recent advances in the synthesis of highly conducting nanocrystalline-diamond thin films and nano wires have lead to an entirely new class of electrochemical biosensors and bio-inorganic interfaces. In addition, it also combines with development of new chemical approaches to covalently attach biomolecules on the diamond surface also contributed to the advancement of diamond-based biosensors. The feasibility of a capacitive field-effect EDIS (electrolyte-diamond-insulator-semiconductor) platform for multi-parameter sensing is demonstrated with an O-terminated nanocrystalline-diamond (NCD) film as transducer material for the detection of pH and penicillin concentration. This has also been extended for the label-free electrical monitoring of adsorption and binding of charged macromolecules. One more recent study demonstrated a novel bio-sensing platform, which is introduced by combination of a) geometrically controlled DNA bonding using vertically aligned diamond nano-wires and b) the superior electrochemical sensing properties of diamond as transducer material. Diamond nano-wires can be a new approach towards next generation electrochemical gene sensor platforms.

This review highlights the advantages of these carbon materials to promote different electron transfer reactions specially those related to biomolecules. Different strategies have been applied for constructing carbon material-based electrochemical sensors, their analytical performance and future prospects are discussed.

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Contents

1. Introduction

In some way, carbon materials touch every aspect of our daily lives. The emerging applications of carbon nanomaterials in electrochemical sensors have lead to production of CNT, Cyrstalline Diamond (CD) and diamond like carbons (DLC) in a large scale. It will soon be possible to take advantage of demanding properties of novel carbon-derived materials to develop a myriad of new applications for chemical sensing. These carbon based materials can be used to operate at wider temperature and longer dynamic range with higher sensitivity even under harsh environmental operating conditions. A range of materials including platinum, gold, and various forms of carbon have thus been found useful for electrochemical detection [1–4]. CNT and diamond are two important polymorphs of carbon that have been widely employed as electrode materials for electrochemical sensing. This review paper mainly focuses on the use of carbon-derived materials, such as CNT and diamonds like NCD and DLC films for electrochemical sensing applications and their implications.

1.1. Carbon nanotubes (CNTs)

The discovery of C_{60} bucky-ball by Smalley's group [5] added a third kind of crystal structure for carbon besides the known forms including graphite and diamond. An analogous kind of crystal structure for carbon i.e., the CNT was found by Iijima [6] in due course of time. Since their discovery in 1991 [6], CNTs have attracted many scientists in the fields of physics, chemistry and materials sciences. CNTs are of tremendous current interest. The structure of CNTs is peculiar and different from graphite and traditional carbon fibers. CNTs are built from sp^2 carbon units, and are seamless structure with hexagonal honeycomb lattices. CNTs have closed topology and tubular structure that are typically several nanometers in diameter and many microns in length. There are two distinct structural families in CNTs, multi-wall carbon nanotubes (MWNTs) [6] and single-wall carbon nanotubes (SWNTs) [7]. MWNTs are composed of concentric and closed graphite tubules. Each tubule is made of a rolled graphite sheet that forms a range of diameters typically from 2 to 25 nm size with 0.34 nm distance between sheets close to the interlayer spacing in graphite. Whereas SWNT is made of a single graphite sheet rolled seamlessly, which is an individual cylinder of 1–2 nm diameter. SWNTs have the tendency to aggregate, usually forming bundles that consist of tens to hundreds of nanotubes in parallel and in contact with each other.

CNTs have unique mechanical and electronic properties combined with chemical stability [8]. They behave electrically as a metal or semiconductor depending on their structure based on their diameter and helicity (symmetry of the two dimensional carbon lattice) [9]. SWNT is a well-defined system in terms of electronic properties and exhibit properties of quantum dots and wires at very low temperature by Coulomb blockade and single electron charging [10]. So far, wide ranges of potential and practical applications of CNTs have been reported, including chemical sensors [11–13], hydrogen energy storage [14], field emission materials [15], catalyst support [16], electronic devices [17], high sensitivity nanobalance for nanoscopic particles [18], and nanotweezers [19]. CNTs have some advantages over other bulky materials because of their small size with larger surface area, high sensitivity, fast response and reversibe at room temperature that also serves as a gas sensor [20,21]. Additionally, CNT possess enhanced electron transfer property when used as electrodes in electrochemical reactions [22], and serves as a good solid support for easy protein immobilization that retains their native activity for use as potential biosensors [23].

The subtle electronic properties suggest that CNTs have the ability to mediate electron transfer reactions with electroactive species in solution when used as an electrode [22]. Therefore, CNT based electrodes have been used in electrochemical sensing [22–26]. Among the traditionally used electrode materials, CNTs showed better behavior than the others which also have good conducting ability and high chemical stability. CNT-based electrochemical transducers offer substantial improvements in the performance of amperometric enzyme electrodes, immunosensors and nucleic-acid sensing devices. The greatly enhanced electrochemical reactivity of hydrogen peroxide and NADH near the proximity or on the CNT-modified electrodes makes these nanomaterials extremely attractive for numerous oxidase- and dehydrogenase-based amperometric biosensors. Aligned CNT “forests” can act as molecular wires to allow efficient electron transfer between the underlying electrode and the redox centers of enzymes. The CNT transducer can greatly influence for enhancing the response of the biocatalytic reaction product and provide amplification platforms carrying multiple enzyme tags.

The CNTs have promising applications in the field of nanoelectromechanical systems (NEMS) that are devices integrating electrical and mechanical components with critical dimensions within 100 nm size [27,28]. CNTs have been considered as a potential alternate for silicon-based circuits due to their attractive electrical properties [27]. The interesting properties of CNTs are associated with their quasi-one-dimensional shape along with sp^2 and π-bonding between the carbon atoms. The π-electrons above and below the hexagonal graphene layer are free to move and form an electron band, producing the semi-metal electrical properties of graphite. However, for the nanotubes, the finite tube circumference restricts the number of allowed electron states. Hence, the semi-metal state of graphene is