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Polymer thin films embedded with metal nanoparticles for electrochemical biosensors applications

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ABSTRACT

Currently, polymer thin films embedded with metal nanoparticles provided the suitable microenvironment for biomolecules immobilization retaining their biological activity with desired orientation, to facilitate electron transfer between the immobilized enzymes and electrode surfaces, better conformation and high biological activity, resultant in enhanced sensing performance. This article reviews focus on various methods for brief discussion of fabrication of metal nanoparticles-polymer hybrid materials and their applications in different electrochemical biosensors. The performance of hybrid materials based electrochemical biosensor can be improved by synergic properties of the metal nanoparticles and polymer network with biomolecules interface via engineering of morphology, particle size, effective surface area, functionality, adsorption capability and electron-transfer properties. These attractive features to hybrid materials are expected to find applications in a new generation of miniaturized, smart biochip devices.

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Abbreviations: MNPPF, Metal nanoparticles-polymers frameworks; MNPs, Metal nanoparticles; AuNPs, Gold nanoparticles; AgNPs, Silver rnanoparticles; PtNPs, Platinum nanoparticles; CuNPs, Copper nanoparticles; CuNFs, Copper nanoflowers; CoNPs, Cobalt nanoparticles; CdSNPs, Cadmium sulfide nanoparticles; FeONPs, Iron oxide nanoparticles; CNTs, Carbon nanotubes; MWCNT, Multi-walled carbon nanotubes; SPEEK, Sulfonated poly(ether-ether ketone); PSf, Poly(sulfone); PANI, Poly(aniline); PPy, Poly(pyrrole); PDDMAC, Poly(diallyldimethylammonium chloride); PVP, Poly(vinylpyrrolidone); PODS, Poly(octadecylsiloxane); PS-*b*-P4VP, Poly styrene block- poly-4-vinylpyridine; PMMA, Poly(methyl methacrylate); PVA, Polyvinyl alcohol; PEDOT, Poly(3,4- ethylenedioxythiophene); PDMA, Poly(*N,N'*- dimethyl aniline); PMPy, Poly(*N*-methylpyrrole); PGA, poly glutamic acid; PPAA, poly(trans-3-(3-pyridyl)acrylicacid); PHM, Poly(hexyl methacrylate); MIP, Molecular imprinted polymer; CT, Chitosan; IPN, Inter-penetrating network; MPTMS, 3-Mercaptopropyltrimethoxysilane; ThPh, Theophylline; AChE, Acetyl cholinesterase; CA, Creatinine amidohydrolase; CI, Creatine amidinohydrolase; SO, Sarcosine oxidase; β-CD, β-cyclodextrin; HAS, Human serum albumin; GO_x, Glucose oxidase; CRP, C-reactive protein; ODN, Oligonucleotide; Cys, Cysteamine; SNPs, Single-nucleotide polymorphisms; GMO, Genetically modified organisms; HRP, Horseradish peroxidise; EP, Epinephrine; DA, Dopamine; ATP, Adenosine triphosphate; AA, Ascorbic acid; UA, Uric acid; SPHINER, Solid-phase-incorporated-reagents; GCE, Glassy carbon electrode; CILE, Carbon ionic liquid electrode; ITO, Indium tin oxide; ISE, Ion selective electrode; SPE, Screen printed electrode; HPLC, High-performance liquid chromatography; AAS, Atomic absorption spectroscopy; CVD, Chemical vapor deposition; RDA, Recommended Dietary Allowances; AI, Adequate Intake; LOD, Limit of detection

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1. Introduction

Metal nanoparticles and polymers frameworks (MNPPFs) have attracted tremendous research interest, as emerging porous materials, in both academia and industry due to their structural diversity, flexibility and tenability as well as high porosity and thus a wide spectrum of applications such as gas storage and separation, selective heterogeneous catalysis, carbon dioxide capture, and guest dependent luminescence, etc (Long and Yaghi, 2009; Ferey, 2008; Liu, 2012; Heilmann, 2002; Ramesh et al., 2009). Interest in metal nanoparticles (MNPs) was motivated by their potential applications of electrochemical sensor (Guo and Dong, 2011), due to their small size (1–100 nm), unique chemical, physical and electronic properties (different from bulk material), flexibility to construct novel and improved sensing devices. Different kinds of nanoparticles are playing diversified roles in different electrochemical sensing systems (Katz et al., 2004). In general, excellent conductivity and catalytic properties of MNPs, make them suitable as "electronic wires" (to enhance the electron transfer between redox centers in target molecules and electrode surfaces), and electrochemical catalysts (due to their nanometer size and structure) (Wei et al., 2012). Metal oxide NPs, may be the semi-conductor NPs, are often used to immobilize target molecules due to compatibility, while other semiconductor nanoparticles based on metal chalcogenides (CdS, CdSe, CdTe) are generally used as labels or tracers for electrochemical analysis (Luo et al., 2006). Now, MNPs based electrochemical sensors and biosensors are playing important role in diagnostic devices (Pingarron et al., 2008; Wang, 2005).

Recently, Bobacka et al. (2003) and Adhikari and Majumdar (2004), reviewed polymers based electrochemical sensor, because of their unique properties of polymers (compatibility, conductive nature, electron promoter and low cost), which are helpful during fabrication of electrochemical sensors and biosensors (Yuan et al., 2012; Revin and John, 2012; Prakash and Shahi, 2011). Till time, single material modified electrodes were not commercialized because of their low sensitivity, poor selectivity, surface poisoning due to adsorbed intermediates and the interference from other species. MNPPFs modified electrodes avoid these problems, which are their attractive features as electrochemical sensors or electrochemical biosensors. Selectivity of electrochemical biosensor depends on the recognizing element (biomolecule, such as antibody) as well as host matrix and interaction between them. MNPPFs are very suitable to achieve the adequate sensitivity and stability, because MNPs act as redox mediator of biomolecules, and polymer acts as selective adsorbate for biomolecules (Ragupathy et al., 2009; Prakash and Shahi, 2011; Gopalan et al., 2009). Contamination of edible items, environment pollution (i.e., heavy metals, explosives, and toxins) and alteration in molecular or ionic concentration (i.e., metabolites, metal ions, hormones, and proteins) in human body are serious health problems. Thus, we need fast/reliable diagnostic tools for biological and chemical species in cost effective manner. Over past three decades electrochemical biosensors has great attendance to medical diagnosis and treatment, such devices easy way to produce the commercialization because of its simple, inexpensive, yet accurate, and sensitive platform for environmental monitoring, industrial quality control, patient diagnosis and treatment. Sensitivity, selectivity, response time, reproducibility, and long life time are highly desirable for electrochemical biosensor performance. Nobel metals, semiconductor (ITO) and carbons (glassy carbon, graphite, and diamond) are potential electrodes for electrochemical biosensors application. Output of electrochemical biosensor must be satisfied in human real samples with cost effective manner (Gubala et al., 2012).

Different electrochemical biosensors have been explored as sensor for diagnosis of genetic disorders like SNPs (Abbaspour and Noori, 2012), pathogens detection (Afonso et al., 2012), forensic applications (Riskin et al., 2008), drug response (Trouillon et al., 2012). Electrochemical biosensor were also applied in food and beverages, (Perez and Fabregas, 2012), GMO content detection in food (Zhao et al., 2011), measuring freshness of food (Ahmed et al., 2008), DNA sensor (Peng et al., 2006), triclosan sensor (Amiri et al., 2007), and other sensors (Kimmel et al., 2012).

In general, MNPPFs based biosensor processes are classified as signal transduction and bio-recognition element methods. Signal transductions are based on electrochemical, optical, thermal, piezo-electric, cantilever and mass sensitive analysis, while bio-recognition element method reveals antibodies (immunosensors), protein receptors, whole cells, nucleic acids and enzymes (Monosik et al., 2012). The electrochemical biosensors are of four types: (i) amperometric- potential is applied between working and reference electrode and the output current is measured continuously; (ii) potentiometric-measurement of charge potential accumulation at the working electrode in compared to the reference electrode in an electrochemical cell during no current flows between them; (iii) conductometric-measurement of variation in conductance/resistance due to the charges produced during enzymatic conversion; and (iv) Impedimetric-monitoring of variation in electrical properties arising from biorecognition events at the surfaces of modified electrodes.

This review focuses on recent advanced on MNPPFs as electrochemical biosensors, their challenge, design and desirable properties as a sensing device employing thin-film growth techniques. Different methods for fabrication MNPPFs, recent innovations and breakthroughs in electrochemical biosensor devices and the need for further frontier research to reach important objectives are also discussed.

1.1. Background

Sensors are devices to convert biological, chemical, or physical changes, into quantifiable and processable electrical signal, by recognizing selective and specific response to target analytes without any interference (Fig. 1). Transducer and detector devices are main component of a sensor. A signal processor collects, amplifies, and displays the signal. A biosensor is an analytical device for the detection of an analyte that combines a biological

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