



Review

Development of biosensor technologies for analysis of environmental contaminants

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ABSTRACT

Recent developments of biosensor technologies for environmental applications are reviewed in this article. Biosensors offer simple, rapid, sensitive and selective detection method for analysis of environmental contaminants mainly including phenols, heavy metals, toxins, pesticides and other organic pollutants. Biosensors, which are usually classified according to the biorecognition elements, e.g., enzyme, DNA, antibody and whole-cell, are discussed respectively. Several examples of their applications for determination of environmental contaminants are reviewed. Special attention will be paid to novel biosensing systems based on new sensing elements and transduction principles. In addition, we present the beneficial use of nanomaterials in constructing biosensors. Finally, a general overview is provided about the future trends, the limitations and challenges in this field.

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1. Introduction

With explosive growth of world population and rapid development of industrialization, the amount of toxic chemicals released into the environment has grown enormously due to frequent human activity. These chemicals in air, water and soil have unknown toxicity and may cause health problems. Environmental pollution has become one of the most acute problems and

naturally captured the world's attentions. Analysis of environmental contaminants is a key step in understanding and managing risks to human health and environment, so there is a urgent need to develop fast and reliable environmental monitoring methods. The increasing amount of potentially harmful pollutants in environment calls for fast and cost-effective analytical techniques. Although highly sensitive and selective, conventional chromatography and spectroscopy analytical methods are time-consuming and laborious when a large number of samples must be screened. Besides, they require expensive equipments, skilled operators and complicated pretreatments. The need for disposable tools for environmental monitoring encourages the development of simple,

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rapid, continuous, cost-effective and field-portable screening methods for analysis of environmental contaminants.

A biosensor is defined by IUPAC as a self-contained integrated device, which is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element (biochemical receptor), which is retained in direct spatial contact with a transduction element [1]. Biosensors can be classified into broad categories, according to the biorecognition element (e.g., enzyme, DNA, antibody, whole-cell biosensor), or the transduction principle (e.g., electrochemical, optical, piezoelectrical, thermal biosensor). Most of biosensors reported in the literature are electrochemical and optical. Electrochemical biosensors are based on selective interaction between target analyte and recognition element, including potentiometric, voltammetric, amperometric and electrochemical impedance spectroscopy biosensors. The interaction can produce an electrical signal that is related to the concentration of the analyte being studied. Optical biosensors are another important subclass of biosensors in which optical transducers respond to the analyte by undergoing a change in their optical properties, such as absorption, reflectance, fluorescence emission.

The history of biosensor began in 1962 with the development of first enzyme based glucose sensing device by Clark and Lyons [2]. There is a rapid development of biosensors over the past 50 years as demonstrated by the large number of scientific publications in this area. In recent years, a growing number of biosensor applications have been developed for environmental analysis [3]. This indicates that biosensor technologies for environmental analysis have become a research hotspot. The main advantages of biosensors are rapid, sensitive, real-time, on-site detection and analysis in the field, thus fulfilling all the requirements for environmental monitoring [4]. As a result, many review articles have been published in recent years discussing the role of biosensors for environmental applications. These reviews are restricted to analytes, such as biosensors for phenols [5], pesticides [6], heavy metals [7] and mycotoxins [8]. Biosensors for environmental applications continually provide a breadth of relevant literatures that is worthy of inclusion in this review. The aims of this review are to discuss recent developments and trends in the use of biosensor technologies for analysis of environmental contaminants within the last 5 years.

2. Enzyme biosensors

The glucose oxidase as the first recognition element was utilized to construct biosensors in 1962. Since then, great efforts have been focused on the development of enzyme-based biosensors for detection of a large range of analytes in clinical diagnostics, food safety and environmental monitoring. A significant number of publications were reported to promote the performances of these analytical devices. The measurement methods by enzyme biosensors are categorized into two types according to the interaction between enzyme molecules and target analytes: (1) if the enzyme metabolizes the analyte, the analyte concentration can be determined through measuring catalytic transformation of the analyte by the immobilized enzyme; (2) if the enzyme activity is inhibited by the analyte, another determination method is to detect the decrease of the enzymatic product formation, and this kind of enzyme biosensor is called as enzyme inhibition-based biosensor.

Pesticides are considered as one of the most dangerous contaminants with high toxicity because of their bioaccumulation and long-term effect on living organisms [6]. A wide range of commercial pesticides are commonly used in agriculture and planting industry. Organophosphate, organochlorine and organo-nitrogen pesticides are the most important groups of pesticides.

The biocatalytic activity of certain enzymes (typically, acetylcholinesterase (AChE)) are inhibited by Organophosphate pesticides (OPs), and the product concentration is also affected. On the basis of this principle, many enzyme biosensors, based on the inhibition of AChE, have been extensively applied to detect OPs in environment. Crew et al. [9] developed a novel automated electrochemical biosensor array based on six AChE enzymes for detection of six organophosphate pesticides (dichlorvos, malaoxon, chlorpyrifos-oxon, chlorpyrifos-methyl-oxon, chlorfenvinphos and pirimiphos-methyl-oxon). Wu et al. [10] have reported a sensitive amperometric AChE biosensor based on mesocellular silica foam (MSF) for the detection of ultra-trace (0.05 ng/mL) monocrotophos. The functioned MSF provided the entrapped AChE a good environment to well maintain its bioactivity. Other organophosphate pesticides (malathion, chlorpyrifos, monocrotophos and methyl parathion) [11,12] and carbamate pesticides (pirimicarb and carbaryl) [13,14] were also detected by electrochemical AChE inhibition biosensors. Fluorescence detection based on enzyme inhibition mechanism was another promising detection method of OPs. The optical transducer of CdTe quantum dots was integrated with AChE by the layer-by-layer assembly technique, resulting in a highly sensitive biosensor for detection of paraoxon and parathion. The detection limits of the biosensors were as low as 1.05×10^{-11} M for paraoxon and 4.47×10^{-12} M for parathion [15].

The most common transduction element associated with enzyme-based biosensors is electrochemical transduction. Oxidase enzymes (typical tyrosinase, laccase and horseradish peroxidase (HRP)) are immobilized on the electrode surface to construct electrochemical enzyme biosensors. Immobilization of enzyme molecules is an important consideration which deeply affects the analytical properties of enzyme biosensors. A lot of innovative immobilization methods and material matrixes have been reported. Yao's group [16] firstly exploited a new and efficient matrix metal-organic coordination polymers (MOCPs) to immobilize enzymes for amperometric biosensing of phenols with high sensitivity. The MOCPs immobilized tyrosinases with high load/activity and mass-transfer efficiency that was ascribed to the inherent porous structure and high adsorbability (Fig. 1). Polycrystalline bismuth oxide [17], SiO₂ sol-gel [18] and poly(ethylene glycol)(PEG) hydrogel [19] were also used as immobilization matrix in enzyme biosensor.

Nanomaterials have attracted considerable attention for the assembling of novel biosensing systems as electron transport mediator and support matrix due to their good conductivity, electrocatalytic activity, high specific surface area, strong adsorption capacity and their ability to be functionalized. Those nanomaterials, such as carbon nanotubes, nanoparticles, graphenes and other nanostructure materials are playing an important role in construction of electrochemical enzyme biosensing systems for environmental applications. Carbon-based nanomaterials, such as graphenes, CNTs and ordered graphitized mesoporous carbons (GMCs) [20] play a significant role in new enzyme biosensor developments. Their remarkable properties, including large surface area, excellent electrical conductivity, high chemical and thermal stability and strong mechanical strength [21], make carbon-based nanomaterials ideal candidates as enzyme support matrix. Carbon-based materials can also be incorporated into nanocomposites so as to couple their unique characteristics with other materials. Recently, an hydrophilic amino acid ionic liquid (AAIL), which possess unique advantages such as good ionic conductivity, wide electrochemical windows and good biocompatibility with enzymes, has been used by our group [22] to combine with GMC for improving the dispersibility of hydrophobic GMC in water phase. The obtained GMC-AAIL nanocomposite displayed better dispersion in the aqueous phase than GMC alone,

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