Journal of Electroanalytical Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

The role of nanomaterials in electroanalytical biosensors: A mini review

Yong Zhang, Qin Wei *

Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong (University of Jinan), School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

ARTICLE INFO

Article history:
Received 29 April 2016
Received in revised form 16 August 2016
Accepted 6 September 2016
Available online xxxx

Keywords:
Nanomaterials
Electroanalytical biosensor
Electrochemical biosensor
Electrochemiluminescence biosensor
Photoelectrochemical biosensor

ABSTRACT

Nanomaterials have been widely applied in the preparation of electroanalytical biosensors. Due to their small size effect, quantum size effect and surface and interface effect, nanomaterials can remarkably improve the important performance indexes of biosensors, such as stability, repeatability and sensitivity. Furthermore, as a result of different composition, morphology and size of all kinds of nanomaterials, they play the different roles in the process of the construction of the biosensors. In this review, the role of nanomaterials in electroanalytical biosensors used as the main line, a summary of 105 articles generalizes the main research achievement of electroanalytical biosensors.

1. Introduction

In recent decades, with the improvement of people life and social productivity, various detection assays have been developed to cope with the challenges of public security and medical test. Among kinds of newly developed analytical assays, the electroanalytical biosensors have numerous advantages, such as good selectivity, high sensitivity, fast analysis speed, low cost, etc. and also can realize on-line continuous monitoring in the complex system [1–5]. Furthermore, the microelectrode in sensor fabrication offers new advantages including high mass-transfer rate, faster sensor response, and ease of integration for parallel analysis [6–9]. The application value of electroanalytical biosensors is more and more important in various fields, for example, food safety analysis, disease diagnosis, environmental monitoring and so on [10–14].

Based on the concept of the biosensor, the electroanalytical biosensors consist of two parts. One is recognizer component for specific identification of target analytes and the other is conversion component for conversion of response signals. According to the different classification criteria, electroanalytical biosensors can be divided into many different types. For example, based on the different mode of signals conversion, electroanalytical biosensors can be divided into electrochemical biosensors, electrochemiluminescence (ECL) biosensors, photoelectrochemical (PEC) biosensors and so on [4,15–17]. Depending on different sensing elements, electroanalytical biosensors can be divided into DNA biosensor, enzyme biosensor, immunosensor, cells biosensor, tissue, molecular imprinting biosensor and so on [18–21]. Whatever types of electroanalytical biosensors, the key goal is to realize the optimization of various performance indicators.

Due to the special physical and chemical properties of nanomaterials, which can be used for improving the adsorption ability of molecules, the signal response speed and the stability of the modified electrodes, the main performance of electroanalytical biosensors, such as sensitivity, repeatability and stability, can be highly improved [22–24]. There has been tremendous growth in the field of nanomaterials-based electroanalytical biosensors.

Here, using the role of nanomaterials in electroanalytical biosensors as the main line, we discussed the application and effect of nanomaterials for fabricating electroanalytical biosensors mainly based on our group's work in nearly five years.

2. Electroanalytical biosensors

An electroanalytical biosensor typically contains three components [25]: (1) the biological element recognizing analyte in the sample (e.g. DNA biosensor, immunosensor, tissue-based biosensor, enzyme biosensor, etc.), (2) the transducer/detector element transforming the signal generated from the biological interaction into another signal which can be more easily measured and quantified (e.g. electrochemical biosensor, ECL biosensor, PEC biosensor, etc.), the associated signal processors primarily responsible for the display of the results in a user-friendly way (e.g. computer, microscopic observation, visual detection, etc.). Generally, different kind of electroanalytical biosensors based on the different mode of signal conversion have the common characteristics, which are fast analysis speed, good accuracy, high selectivity and sensitivity, etc. On the other hand, due the different transducer parts, whatever of electrochemical biosensor, ECL biosensor and PEC biosensor, has its own characteristics and advantages. Herein, we only discuss these three kinds of biosensors and the role of nanomaterials playing in them (Fig. 1 and 3).

* Corresponding author.
E-mail address: sdjndxwq@163.com (Q. Wei).

http://dx.doi.org/10.1016/j.jelechem.2016.09.011

2.1. Electrochemical biosensors

Electrochemical biosensors are of special interest due to their analytical characteristics including operational simplicity, extraordinary sensitivity, low cost and rapid, real-time detection [26–28]. Furthermore, electrochemical biosensors can be prepared for point-of-care device [13]. In recent years, intensive research effort has been put into the design of novel electrochemical biosensors as well as the improvement of their performances [29–31]. However, the electrochemical biosensor still faces many challenges. For example, based on their inherent flexibility, sandwich enzyme-linked immunosorbent assays (ELISA) have emerged as the method of choice for protein quantitation in clinical and research laboratories, but these heterogeneous assays require expert users with dedicated instrumentation, and they are time-consuming, laborious, and expensive [13]. To overcome the difficulties, as shown in Table 1, kinds of novel nanomaterials with excellent properties have been synthesized and applied in fabrication of electrochemical biosensors, which will be discussed in the following third parts.

2.2. ECL biosensors

ECL is a powerful analytical technique due to its high sensitivity, wide linear range, low background and simple instrumentation, which has been deeply studied and extensively applied to various fields including analysis of food or pharmaceutical, DNA-aptamer, immunoassay and so on. As for the ECL system (e.g. as shown in Fig. 2), two reaction procedures were included: the first step is the diffusion of generated reactive species from electrode and the second step is the emission of light which was induced by the reaction between electrogenerated substances and co-chemicals [32–34]. At present, the biggest challenge of fabricating ECL biosensor is increasing the efficiency of the core electron–hole recombination of nanomaterials and thus the luminescent emission, which can get high sensitivity for ECL detection [33]. For this purpose, as shown in Table 1, different kind of nanomaterials were used for preparation of ECL biosensors.

2.3. PEC biosensors

Like the ECL analytical technique, the PEC technique is also the evolutionary generation of the electrochemical method [3,35]. It also naturally inherits the advantages of the above techniques, such as low cost, simple instrumentation and high sensitivity. However, a great difference exists between them and the PEC technique offers some merits that could not be accomplished on the conventional platform. In PEC detection, light is utilized to excite the photoactive species and the electrical signal is transduced as the detection readout, which is the reverse of ECL [36]. Using two separate forms of signal for excitation and detection, this technique possesses potentially higher sensitivity because of the reduced background associated with it [3,37–38]. Actually, for the detection of identical analytes with the same configurations, the PEC routes usually exhibit superior detection properties (e.g., lower detection limits) than their electrochemical counterparts [39]. Due to its desirable advantages and attractive potential in future biological analysis, the popularity of PEC bioanalysis has grown tremendously among the analytical community.

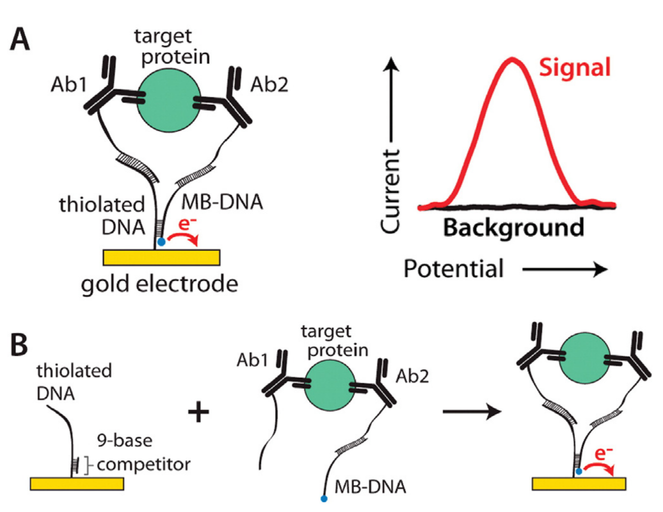

Fig. 1. The schematic illustration of the sandwich-type electrochemical immunosensor [13].

3. The role of nanomaterials

Over the past few decades, considerable advances have been made in electroanalytical biosensing area due to the tremendous progress in nano-research and the unique characteristics of nanomaterials [22,40]. The development of nanomaterials promotes the progress of electroanalytical biosensors in various aspects.

3.1. Selectivity promotion

On the basis of the chosen bio-recognition elements aiming at different targets, various electroanalytical biosensors have been proposed for particular analytical purposes. The most two general models of the electroanalytical biosensors may be demonstrated by the simplest protocol of biotin–avidin recognition [3] and enzymatic biosensing. Whatever model of the electroanalytical biosensor, to immobilize the biomolecule, such as antibody, DNA, and enzyme, is the first challenge for fabricating biosensor. Considering the biological activity of the biomolecule, nanomaterials applied for biosensing should not only have large capacity of biomolecule adsorption, but also be biocompatible. According to the structure of nanomaterials, 0 dimensional (D), 1D, 2D and 3D nanomaterials play different roles for kinds of electroanalytical biosensors.

3.1.1. 0D nanomaterials

Quantum dots (QDs) as the delegate of 0D nanomaterials are always applied for biosensors in two ways, i.e. modified on the electrode directly and modified on the DNA or antibody as the label. Whatever ways they are applied, 0D nanomaterials are used to get or enlarge the signal [41]. In general, QDs are made of elements in groups II-VI or III-V in the periodic table. They are known for their small size (1-10 nm) and size-dependent optical-electronic properties, low toxicity, environmental friendliness, low cost and facile synthesis [27]. As a representative of the typical QDs, CdS QDs can be modified on the electrode to immobilize ds-DNA and due to the energy transfer, occurs between the excitons in the QDs and plasmons in the metal surface, the ECL properties of QDs near the metal surface could be improved significantly by adjusting the distance between nanostructural metallic surface and QDs [42].

Furthermore, due the high optical absorption coefficients, heterostructures based II–VI group compounds nanoclusters, e.g. CdX (X = S, Se or Te), are suitable materials used for fabricating thin-film photovoltaic device, solar cells and photo conductors. Although they have good photoelectron conversion efficiency, the rapid photo-generated electron–hole recombination rate of CdX results in a decrease in the photocurrent density. For getting high performance of PEC sensing device, we found ternary CdZnS thin films often exhibit improved chemical, structural and optical properties, and could be appropriate photoactive materials with high charge separate coefficients. We used them as an ideal photoactive material in PEC sensing for the detection of two metal ions on the same sensing platform [43].

However, Cd-containing QDs are always shown deleteriousness for biosensors. For reducing the toxicity of Cd-containing QDs, carbon