Application of Electrochemical Biosensors for Chemical Hazards Detection

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Abstract. Electrochemical biosensor is a subject that has received the most attention from scientists in recent years. It is not only related to human life but also natural environment. Research on electrochemical biosensors is also cross-linked with many other scientific fields, such as nanomaterials and hazardous chemical detection. In this research, electrochemical biosensor is discussed by divided into three types, including potentiometric, amperometric, and voltammetric biosensors. The unique mechanism, advantages and application of these electrochemical biosensors is also introduced in this article. Potentiometric biosensor is frequently used for phosphate, toxicity and heavy metal detection. Amperometric biosensors are usually combined with enzymes for the identification of additives in products and contaminants in water. Voltammetric biosensors are most commonly used for blood glucose testing, but can also detect many tastes.

Keywords: Electrochemical biosensor, Application, Detection, Chemical hazards.

1. Introduction

With the development of technology and globalization, people are no longer satisfied with simple survival but have a higher demand for the quality of life. However, at the same time, under the development, a large number of harmful substances are emitted, some of which can be seen visually, while most of them are very small and hard to see with eyes. Among them, the most concerned is the impact of hazardous substances on the ecological environment and public health.

Storm surges, disaster waves, sea ice, red tides and tsunamis are usually been regarded as the five major disasters. However, what people don’t see is the most frightening. For example, marine pollution caused by heavy metals and radionuclides. Illegal discharges of municipal sewage bring bacteria and pathogens into the ocean. However, these hazards are also highly unappreciated by humans because the optical properties and electromagnetic characteristics of the ocean are not easily detected [1]. Food safety is strongly correlated with human health. Since there are too many of the same type of food on the market, suppliers add many additives to their recipes in order to attract consumers. If Additives are safe, food formulations are reasonable, both are poorly to be identified by the naked eye. Therefore, biosensor is the most widely used machine to deal with hazards detection problems. A general biosensor is composed of the following components: analyte, bioreceptor and transducer. Analyte is the substance that needs to be detected. Bioreceptor is generally a molecule that is used to identify the analyte. Transducer interacts with analyte-bioreceptor to transfer the recognition in bioreceptor into a signal. Electronics are used to convert and condition the analog signals into digital signals for quantization in the display unit. Display unit generates numbers, graphs, and curves from signal processing as customers require [2].

Here are some reasons that why biosensor is the most useful machine to detect hazards, because of its high sensitivity, reproducibility, sensitivity and intelligibility. Biosensors are highly selective due to the selective recognition of molecular structures of biological substances by enzyme membranes, mitochondrial electron transport system particle membranes, microbial membranes, antigen membranes, and antibody membranes, which are catalytically activated only for specific reactions. The sensor is not contingent, and each time when the same substance is measured, the result that occurs is within the mean available error range. It allows the sensor to be accepted for each result. The sensors widely used in the market are very sensitive, which means that they can accurately detect even very low of the component being detected in the sample. For example, a prostate-specific antigen (PSA) concentration of 4 ng/mL in the blood is associated with prostate cancer [2]. Doctors will suggestion if to do more accurate tests according to biosensor result. The result of biosensor is usually showed as a linear graph. the intensity is increase with the increase of concentration. It's convinced for customers to read out their result. In addition, biosensor only need very few times to deal with sample. It's very convinced for patient to find their result in a short time. There are various types of biosensors.

According to the principle of sensor device detection, it can be divided into: thermal biosensor, field-effect tube biosensor, electrical biosensor, enzyme electrode biosensor, etc. In this article, different types of electrical biosensors will be discussed in detail. The electrochemical biosensor mainly uses a solid electrode as the base electrode and fixes the biological activity as a molecular identifier on the electrode surface, then the target molecule is captured on the electrode surface by the specific recognition between the biological molecules, and the base electrode converts the concentration signal into a measurable electrical signal such as potential, current, resistance or capacitance as the response signal, thus achieving quantitative or qualitative analysis of the target analyte [3].

Electrochemical biosensors are widely used in the medical health food industry and agriculture because of their high sensitivity and miniaturization. Compare with other types biosensors, electrochemical biosensor transfers the signal to electrical signal, which is mostly to be measured. Because ammeter voltmeter technology has been perfected and is a visualization technique that is accurate to decimal places. By simplifying the circuitry and reducing the power and board size, the portability of electrochemical sensors can be improved [3]. Also, because of the unique nature of electricity, the connection between sensors and other electronic devices is realized, making real-time monitoring possible.

2. Three types electrochemical Biosensors

2.1. Potentiometric electrochemical biosensor

Potentiometric electrochemical sensing is a direct electrochemical approach which is portable, low cost to manufacture and operation which is also provide immediate response. In a potentiometric system, the potential of an electrochemical cell is measured under resting conditions. In potentiometric system, the current is not used or only a very weak current is used to flow through the electrochemical cell. This difference is helpful in ensuring that the analyte composition remains constant during the measurement.

The electrochemical cell in the potentiometric system consists of two cells. The potential of the cell in which the cathode is located is subtracted from the potential of the cell in which the anode is located to obtain the potential of the entire electrochemical cell. The potential is varied according to the number of ions passing through the membrane as the analyte concentration varies [4].

The selectivity of a potential system for electrochemical determination of cations, anions or biological materials depends on the capability of the membrane material used to make the potential sensor. Figure 1 shows the mechanism of potentiometric electrochemical biosensor with nanomaterials as labels [5]. Potentiometric electrochemical biosensor can be used in several aspects. Take phosphate as an example. Phosphates are widely used in food processing as an important food ingredient and functional additive. Furthermore, phosphorus plays a critical role in photosynthesis in plants, which is why many fertilizers contain phosphorus. But unregulated phosphorus use can lead to global eutrophication and severe water pollution. Traditional method to detect the concentration of phosphate is quantitative analyzed in laboratory. But the process is complex and costly. Cobalt is a robust heavy metal that exhibits a very high selectivity for phosphates. Cobalt oxide adsorbed on the surface of the electrode after pretreatment CoO provides cavity as host and receives $H_2PO_4^-$ as its guest. The potential is modified by the change of dissolved oxygen in $H_2PO_4^-$ at the Co electrode.

However, it is worth noting that cobalt is highly selective for phosphate only under acidic conditions [4].

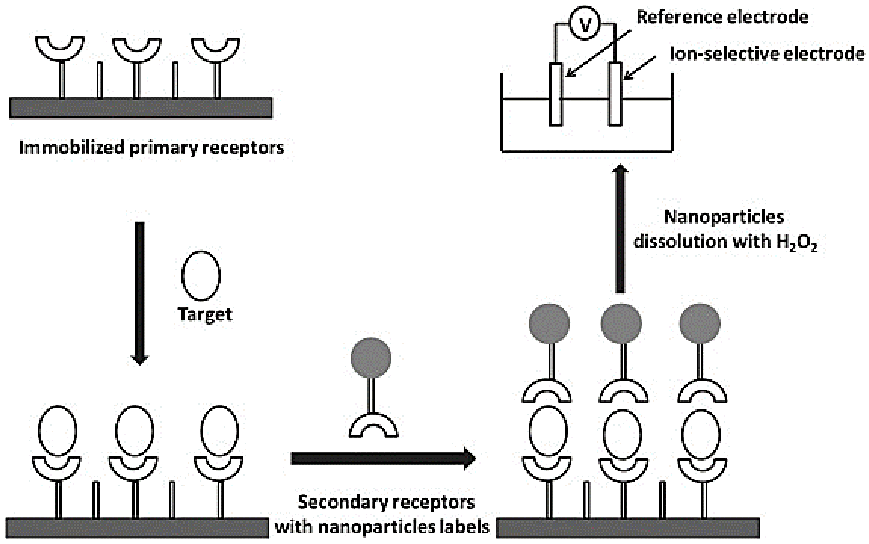

Figure 1. The principle of potentiometric electrochemical biosensor [5].

Potentiometric biosensors can also be used to determine toxicity. Due to increased environmental controls in recent years, the toxicity of industrial wastewater needs to be qualified before it can be discharged. Potentiometric sensors are used to perform this test according to the reproducibility of the experiment, the organisms used to determine toxicity should be fast-growing, vigorous and inexpensive, with ammonia oxidizing bacteria (AOB) as bioreceptors and European nitrosomonas as polymeric membrane. Ammonium selective electrodes as detectors can be used to detect toxicity in water. The toxin has an inhibitory effect on AOB activity where AOB cells are fixed on a mounted electrode holder. Toxicant concentration and toxicity were obtained by measuring ammonium consumption rate through molecular recognition and transduction ammonium selective membrane electrodes [5].

The most significant function of the potentiometric electrochemical biosensor is to detect heavy metal particles. In terms of environmental pollution, heavy metals are mainly referred to mercury (mercury), cadmium, lead, chromium and others. Heavy metals are very hard to be biodegraded, instead they can be enriched thousands of times by the biomagnification of the food chain because they can react with protein to produce complex and finally enter the human body [6]. The potentiometric methods commonly used to detect heavy metals are lab-on-a-chip (LOC) and microfluidics technologies. The membrane is generally made by plastic polymer. Polyvinyl chloride is acted as a polymer matrix, and ionic groups with high selectivity for heavy metal ions are immobilized in the compound matrix. Take lead (II) ions as an example. An oxy-diamides potentiometric electrode is developed which is only exhibited high lead (II) selectivity. However, lipophilic lariat crown ethers have been found to act as high selectivity electrode not only for lead (II) ions but also other heavy metal ions. Therefore, lipophilic lariat crown ethers are more widely used to detect heavy metal ions [7].

Potentiometric biosensor is a good type of electrochemical biosensor, but most of them are still sensitive to temperature and pressure. Furthermore, conductive polymers and potentiometers tend to form water films that affect detection accuracy. Therefore, Potentiometric biosensor should be studied in more depth. For example, it is necessary to investigate new electrode materials from high surface area nanomaterials and hydrophobic organics.

2.2. Amperometric electrochemical biosensor

Amperometric biosensors not only offer the same high sensitivity, fast response and low-cost features as other electrical sensors, but also have the advantage of a wide linear range and low detection limits. It has low detection limits because it can accurately detect at very low concentrations. When a sample is received for testing, it can be diluted to obtain more samples for repeated testing to obtain accurate results. Aiming for direct quantification of target analytes is made possible by the high specificity and wide linear dynamic range. The amperometric method is based on a fixed voltage and dynamic measurement of the current generated by the determination of electrochemical oxidation or reduction depending on the concentration of the substance to be measured. Three electrodes are also generally required, a working electrode, which maintains a constant potential, a reference electrode and an auxiliary electrode. The working electrode is a metal or carbon-based material. Enzymes are also indispensable in amperometric biosensors. Enzymes fixed in the transducer should provide a stable surface for the immobilization of biomolecules while preserving their structure and mobility [8]. Figure 2 shows the mechanism of ameperometric biosensor.

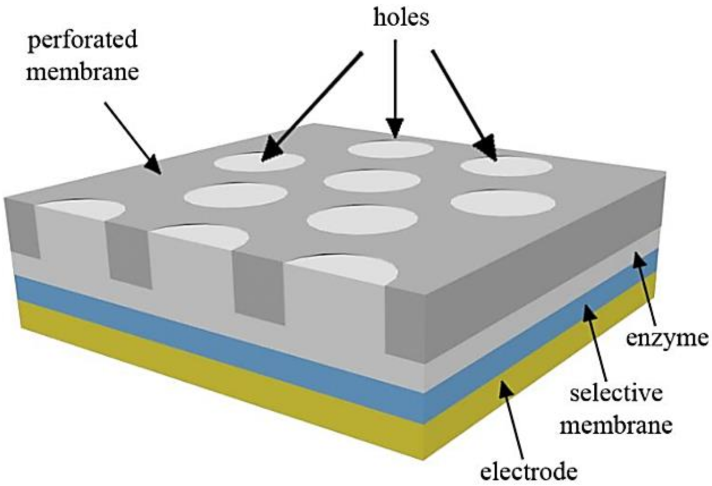

Figure 2. The principle of ameperometric biosensor [9].

It illustrates various regions of the biosensor. The enzyme-catalyzed reactions occur in the enzymatic region. In the selective membrane, the production assay process is performed. Finally, in the electrode, the movement of electrons in the redox reaction occurring in the enzyme is converted by the sensor into an output current [9].

Amperometric biosensors are most widely used in food testing, and one example is the amperometric lactate sensor. How to tell which step of fermentation is reached basically depends on the measurement of lactic acid levels. Lactic acid can also be used to detect the freshness and stability of the food and thus set the shelf life. Lactate oxidase (LOx) is a globular flavoenzyme. Which is fixed in the working electrode. Oxidation of L-lactate to pyruvate catalyzed by LOx Formation of H_2O_2 in the presence of dissolved oxygen. According to the report, LOx works very well. The biosensor current is strongly related to the concentration of L-lactate. Moreover, interference of electroactive substances is avoided because of the high working potential [8].

Phenol-containing compounds are a very serious source of water pollution. Amperometric biosensors are also widely used today to detect the concentration of phenolic compounds. In this amperometric biosensor, coriolus hirsuta laccase (ChL) is used as the enzyme. Fixed ChL in the working electrode which is made of multiple wall carbon nanotubes. This will result in a more even distribution of enzymes. Based on the experiment result. The maximum current response is shown in electrostatic absorption technique. At the same time, it can also use repeatedly, after ten times the maximum current response value reached 90 percent of the original. It concluded that, carbon nanotube-based amperometric biosensor is suitable to detect the phenol-containing compounds concentration, because of high current response and reusability [10].

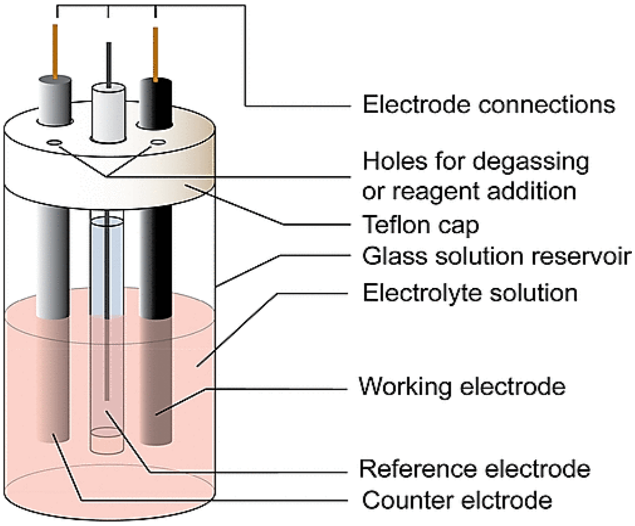

Figure 3. The principle of voltammetric biosensor [14].

One of the most interesting aspects of the amperometric biosensor is that based on its principle a microbial biofuel cells (MFC) can be produced. This is a very advanced and green technology. Because it can generate electricity while treating wastewater through the degradation of some pollutants and enzymes. In the MFC designing process, it is very critical to choose the method of fixing the electrode surface. Idealized fixation of cells ensures high cell motility and prevents cell leakage. It removes nutrients and metabolites from the solution to be tested. Ensures electrons transfer from cell to electrode. One of the best fixed method is created form the amperoteric biosensor. Based on the porous structure of polyacrylamide, while having beads with positively charged groups, it facilitates good adsorption of *E. coli* cells on the surface. The anode material is also important as it affects the charge transfer efficiency of the biomaterial. This is a limiting factor for the sensitivity of amperometric biosensors or the efficiency of MFCs. Semipermeable membrane is a feasible choice [11].

2.3. Voltammetric electrochemical biosensor

Voltammetric electrochemical biosensor is the most common biosensor in our daily life. Both voltammetric and amperometric biosensors require a potential to be applied to the working electrode and the reference electrode, as shown in Figure 3. For the amperometric biosensor, however, its reference voltage is constant. The working electrode operates at a constant voltage and the concentration is analyzed by detecting changes in the current function. Consequently, amperometric biosensors can be considered as a branch of voltammetric biosensors. Voltammetric biosensors measures current according to the varies of potential which is scanned over a set potential range [12].

Most voltammetric biosensors use a standard three-electrode configuration. When a voltage is applied to the working and reference electrodes, the current signal is measured between the working and counter electrodes. In attempt to retrieve as much information as possible from the solution, combinations of a set of pulses can be grouped together at regular intervals to form a waveform as an applied potential, and more information can be obtained by using dissimilar types of working electrodes [13].

Take a glucose sensing at Con AeC60 eTOABþ/GCE sensor as the example to briefly explain the mechanism. Figure1 illustrate due to the high specific affinity of glucose for Con A immobilizes it on the electrode surface to provide molecular binding sites for reversible redox in aqueous solutions. Thus, the change in current at the working electrode is monitored.

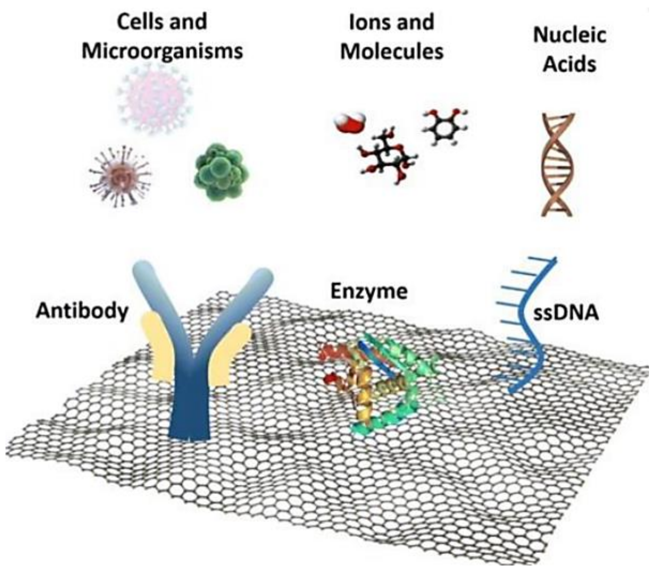

Figure 4. The principle of graphene-based biosensor [15].

The final image shown in display unit is the cyclic voltammograms. It is very important in this technique. It is comparable to the current vs. potential diagram. Generally, most experiments do not achieve such ideal images. In this illustration, in the forward scan, the potential is swept negatively from the starting potential E1 to the switching potential E2. This is referred to as the cathode trace. Then the sweep direction is reversed and the potential is swept positively to E1, referred to as the anode trace [14]. Since it allows for rapid redox behavior over a wide potential range, it is possible to clean and monitor the aptamer on the electrode surface. As a result, it has cleanliness, repeatability and stability [12]. Although there are many studies on blood glucose meters, basically all blood glucose meters are based on voltammetric biosensors in depth.

Taking synthesized graphene electrodes non-enzymatic glucose biosensor as an example. Graphene is a hexagonal planar material with two-dimensional (2D) carbon nanomaterials. Graphene does not contain metal impurities and is easier to bond to electrodes than CNTs. Non-enzymatic glucose biosensors are designed to oxidize glucose depending on the activity of electrocatalysts. Catalysts such as metals (Au, Ni, Cu, Pd, etc.), metal oxides (CuO, RuO_2, etc.) The graphene-based nanocomposites are widely used in non-enzymatic glucose sensors due to their distinct properties, sensitivity, cost effectiveness and environment friendly, as shown in Figure 4. However, the lack of portability and the high demand for graphene purity are problems waiting to be solved [15].

Voltammetric biosensors can be used as tongue to detect many flavors, such as bitter, salty and acid. The bitterness was mainly derived from $MgCl_2$, using CV based approach with extra virgin olive oil as working electrode. The results have demonstrated the signal acquired by the tongue and the bitterness score bitter given by the expert panel related strongly. Salt taste mainly comes from NaCl in food, electrodes made up of precious and non-precious metals (such as gold, iridium, platinum and rhodium) allow detection of chloride ion concentration. The acidity generated from hydrogen ions in hydrochloric acid and acetic acid. The most critical electrodes for acid prediction are Ni and Ag for simple solution, and Ag and Ir for binary solution [13].

3. Conclusion

To sum up, the development of electrochemical biosensors is necessary because too many pollutants that are harmful to organisms as well as to the environment have been created due to rapid industrialization. But it is not possible to quantify them by the naked eye. Electrochemical biosensors are the most widely used category in today's society because they have the advantages of high selectivity, high sensitivity, portability, reproducibility, and easy signal processing, including potentiometric biosensor, amperometric biosensor and voltametric biosensor. The potentiometric biosensor measures potential without passing current, which is helpful in ensuring that the analyte composition remains constant. Amperometric biosensor measures current according to a fixed potential, which is beneficial to detect at very low concentration. Voltametric biosensor is the most widely used biosensor and it can measure current according to varies potential. Dynamic changes can be observed at each moment and the results are more accurate. However, there are still some difficulties of application of electrochemical biosensor that needed to be solved by scientists. For example, it is sensitive to temperature and has a limited shelf life.

Authors' Contributions

Yunjie Wang completed the work design and article writing.

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