Nanomaterial-based electrochemical hydrogen peroxide biosensor

Abstract

Hydrogen peroxide (H$_2$O$_2$) is well-known oxidizing, bleaching agent and also one of the significant by-products of diverse regulating biological processes. It has been recognized as a threat in the progression of atherosclerosis, renal disease, ageing and other diseases. Hence, determination of H$_2$O$_2$ in trace levels in biological samples is of great importance. This article briefly reviews the electrochemical detection method for hydrogen peroxide sensing, including the nanomaterial based enzyme-containing and non-enzymatic biosensor. The biosensor can achieve microscopic detection of hydrogen peroxide. It also discusses the performance and future prospects of the electrochemical H$_2$O$_2$ biosensor.

Keywords: hydrogen peroxide, bleaching agent, biosensor, electronic technology, medical hygiene, biomedical science, carbon nanotubes, graphene, molybdenum disulfide, Au nanoparticles, polyaniline

Abbreviations: H$_2$O$_2$, hydrogen peroxide; HRP, horseradish peroxidase; CAT, catalase; LOD, outstanding detection limit

Introduction

Hydrogen peroxide (H$_2$O$_2$), a strong oxidizing agent and essential intermediate, is easily miscible with water and extensively utilized in light industry, electronic technology, medical hygiene, biomedical science and pharmaceutical engineering. Therefore, the rapid, reliable and accurate determination of hydrogen peroxide is of highly importance in the fields of food security, environmental protection and bioanalysis. Consequently, various kinds of H$_2$O$_2$ detection and measurement methods have been developed, such as fluorometry, cell imaging, spectrophotometry, and electrochemical analysis. Among the above-mentioned methods, the electrochemical detection technology is considered to be the most promising approach because of its excellent advantages including rapid response, convenient operation and high sensitivity. Usually, the nonenzymatic and enzymatic H$_2$O$_2$ biosensors are the most commonly used electrochemical detection method.

Discussion

Enzyme-based biosensor

Until now, many studies on this subject have focused on enzyme-based H$_2$O$_2$ biosensor, which has the advantages of high efficiency and good selectivity. Horseradish peroxidase (HRP) and catalase (CAT) are the two kinds of enzymes that are commonly used for H$_2$O$_2$ detection. However, the immobilization and stabilization protocol of the enzyme are complicated, and it is difficult to achieve the direct electron transfer on bare electrode. Then, the excellent support materials are developed, which provide better environment for loading the enzyme efficiently and promote direct electron transfer. Therefore, carbon-based nanomaterials, metal nanoparticles and polymer have been prepared and were used in fabricating enzyme-based H$_2$O$_2$ biosensors. The introduction of nanomaterial can increase the enzyme loading area, contact with more detectors, and enhance electron transfer rate. The nanomaterials, such as carbon nanotubes, graphene, molybdenum disulfide, Au nanoparticles, polyaniline and their hybrid nanostructure can improve the performance of the biosensor effectively. Table 1 shows various enzyme-based H$_2$O$_2$ biosensors, which usually possess outstanding detection limit (LOD) but low sensitivity and narrow linear range. In addition, due to the intrinsic nature of enzymes, the enzyme-based biosensors inevitably suffer from environmentally instability, high cost and complicated immobilization procedure.

Non-enzymatic biosensor

Previous works have shown that the non-enzymatic electrochemical biosensor can well avoid the disadvantages of instability and poor reproducibility, providing an effective way for hydrogen peroxide detection. The non-enzymatic biosensor is based on the electrocatalytic reduction, and the reaction is performed on the surface of the electrode. The electrochemical detection using conventional electrodes requires a relatively high over-potential. Efforts were then devoted to the minimization of over-potentials by using nanomaterialer modification. Experimental results demonstrate that the nano electronic medium can improve the electron transfer rate and enhance the anti-interference ability of the biosensor.

The transition metal oxide, such as CuO, MnO$_2$, and Co$_3$O$_4$, exhibits electrocatalytic performance towards H$_2$O$_2$. This type of nanomaterial has the advantages of low cost, environmental friendly and easy to prepare. However, its stability and sensitivity are unsatisfactory. Therefore, the noble metal based non-enzymatic H$_2$O$_2$ biosensor caused more attentions. Among them, the Ag possesses a better property for H$_2$O$_2$ reduction due to the unique electronic and catalytic properties as well as its good stability. Nevertheless, the strong van der Waals force between Ag nanomaterials can cause aggregation, resulting in performance degradation. In response to this problem, various support nanomaterials, such as graphene, poly microparticles, carbon nanodots, and amorphous carbon are used for immobilizing Ag nanomaterials, which are confirmed to be an effective strategy for improving the sensing properties of the as-prepared biosensors. Furthermore, we summarized various Ag nanomaterial based non-enzymatic H$_2$O$_2$ biosensors in previous reports, as shown in Table 2. These biosensors exhibit excellent sensing characteristics for H$_2$O$_2$ determination which can be attributed to the superior electrocatalytic of Ag and synergistic effect between the nanomaterials.
In summary, with the development of nanoscience and nanotechnology, many kinds of nanomaterials have been introduced to fabricate electrochemical $H_2O_2$ biosensors. And also the performance of the biosensors has been greatly improved. The enzymatic biosensor exhibits very low detection limit, which is suitable for biomedical applications. Compared with enzyme-based biosensor, the non-enzymatic $H_2O_2$ biosensor usually possesses a larger linear range and better sensitivity, and it is more applicable to industrial and environmental monitoring. Furthermore, the Ag nanomaterial based non-enzymatic biosensor is worthy of our more research due to its excellent properties and broad application prospects. Although there are encouraging progresses in electrochemical $H_2O_2$ biosensors, several limitations, such as preparation process, reproducibility and reliability, needs to be addresses before these sensors can be used for routine diagnosis in the field.

### Acknowledgements

This project was supported by grants from the Guangdong Natural Science Foundation (No. 2016A030313734, 2016A030313735).

### Conflict of interest

The author declares no conflict of interest.

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### Table 1 Various enzyme-based $H_2O_2$ biosensors

| Type of biosensor | LOD (nm) | Linear range (mM) | Sensitivity | Reference |
|-------------------|----------|--------------------|-------------|-----------|
| CAT/PL/I-MWCNT/GCE | 8        | 1n-3.6μM          | 0.39μA·mM$^{-1}$·cm$^{-2}$ | Vilian AE et al. $^{19}$ |
| NF/CAT/MWCNTs-COOH/Cys-AuNPs | 0.5      | 1μM-1μM          | --          | Hong J et al. $^{13}$ |
| CAT/MoS$_2$-Au     | 100      | 0.5μ-0.2mM       | 0.18μA·mM$^{-1}$·cm$^{-2}$ | Shu Y et al. $^{12}$ |
| PANI/CAT/glutaraldehyde | 2.18μM  | 5μ-0.1mM        | --          | Akyılmaz E et al. $^{11}$ |
| HRP/Graphene       | 0.026    | 80n-0.66μM      | --          | Liu SQ et al. $^{11}$ |
| HRP-Au-CPE         | 210      | 0.48-50μM      | --          | Liu SQ et al. $^{14}$ |
| HRP-Au thin-film gold | 16μM    | 20-500μM       | 12μA·mM$^{-1}$·cm$^{-2}$ | Golsheikh et al. $^{17}$ |

### Table 2 Various Ag nanomaterial based non-enzymatic $H_2O_2$ biosensors

| Type of biosensor | LOD(μm) | Linear range (mM) | Sensitivity | Ref. |
|-------------------|---------|--------------------|-------------|------|
| AgNPs/C-CPE       | 0.3     | 0.1-17            | 309.4μA·mM$^{-1}$·cm$^{-2}$ | Zou YS et al. $^{18}$ |
| AgNPs/MWCNT/GCE   | 0.5     | 0.05-17           | 1.42μA·mM$^{-1}$ | Zhao W et al. $^{18}$ |
| AgNPs-rGO/ITO     | 5       | 0.1-100           | --          | Golsheikh AM et al. $^{23}$ |
| PQ11-AgNPs/GCE    | 33.9    | 0.1-180          | --          | Lu W et al. $^{24}$ |
| AgNPs/PVA/Pr      | 1       | 0.04-6           | 128μA·mM$^{-1}$ | Lu W et al. $^{25}$ |
| AgNPs-rGO/GCE     | 4.3     | 0.1-70           | --          | Guascito MR et al. $^{26}$ |
| AgNPs-PMPD/GCE    | 4.7     | 0.1-30           | --          | Golsheikh AM et al. $^{27}$ |
| AgNPs-NFs/GCE     | 62      | 0.1-80           | --          | Tian J et al. $^{29}$ |
| AgNPs-Co3O4-rGO   | 0.035   | 0.1μA-7.5         | 146.5μA·mM$^{-1}$·cm$^{-2}$ | Wu Q et al. $^{29}$ |
| ErGO-Ag/GCE       | 1.6     | 0.1-100           | --          | Golsheikh et al. $^{42}$ |
| AgNPs-MWCNT-rGO/GCE | 0.9     | 0.1-100         | 833μA·mM$^{-1}$ | Lorestani F et al. $^{41}$ |
| N-graphene-Ag NDS/ITO | 0.26   | 0.1-80         | 88.4μA·mM$^{-1}$·cm$^{-2}$ | Tajabadi MT et al. $^{42}$ |

### Citation

Zhao Z, Ou Q, Yin X, et al. Nanomaterial-based electrochemical hydrogen peroxide biosensor. *Int J Biosen Bioelectron*. 2017;2(3):100–102. DOI: 10.15406/ijbsbe.2017.02.00027
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