Sensors and Actuators B 242 (2017) 718–727

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Acidification of manganese dioxide for ultrasensitive electrochemical sensing of hydrogen peroxide in living cells

Wushuang Bai, Xinjin Zhang, Sai Zhang, Qinglin Sheng*, Jianbin Zheng*

Institute of Analytical Science, Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, China

ARTICLE INFO

Article history:
Received 18 August 2016
Received in revised form
15 November 2016
Accepted 23 November 2016

Keywords:
Manganese dioxide
Hydrogen peroxide
Acidification
Electrochemical biosensing
Cell

ABSTRACT

Nanomaterials have been used widely for electrochemical analysis in biological system in recent years. In order to cover the shortage of singular materials, composite nanomaterials were provided, but in the meanwhile laborious synthetic procedures and complex analytic mechanism has to be faced. In this work, for the first time, one-step acidification of flower-like manganese dioxide (MnO_2) was performed to modify its catalytic reactive and active crystalline facets, and nonenzymatic electrochemical sensor was fabricated based on the singular materials to detect hydrogen peroxide (H_2O_2) released from living cancer and normal cells. According to the SEM, XRD characterizations and electrochemical investigations, it was found that 001 and 002 facets probably be the reactive facets while 111 and 020 facets are active facets. Meanwhile, the obtained sensor exhibited a low detection limit of 0.02 μM, a fast response and a wide linear range of 0.00008-12.78 mM which can be applied successfully for quantitative detection of H_2O_2 released from living cells in stimulation of AA. The work provides a simple and efficient electrochemical biosensing platform based on modification of crystalline facets of metal oxide. Considering the good sensing property, simple catalyst synthesis and analytic mechanism, its potential uses can be exploited for analytic, catalytic, physiological and pathological studies.

© 2016 Elsevier B.V. All rights reserved.

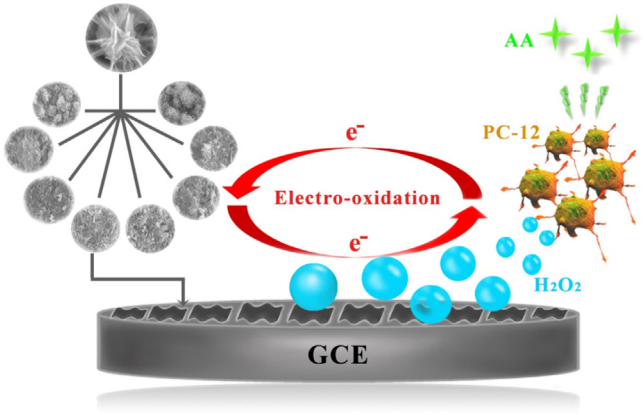
1. Introduction

Reactive oxygen species (ROS) are important molecules which regulate the DNA damage, protein synthesis and cell apoptosis, and accumulation of ROS will lead to various diseases such as cancer, diabetes, neurodegenerative Alzheimer's diseases, etc [1–3]. Therefore, determination of cellular ROS is significant for clinical and biological studies. Hydrogen peroxide (H_2O_2), formed by disproportionation of unstable reactive oxygen species superoxide ions, is the most representative one which can penetrate into other cellular compartment due to its long life time [4–8]. Therefore, fast, sensitive and quantitative detection of intracellular H_2O_2 is full of challenge in state of the art. In recent years, various methods have been used for detection of H_2O_2 such as fluorescence, chemiluminescence, mass spectrum, electrochemical strategy, etc [9–14]. Among these methods, electrochemical strategy, especially electrochemical sensing, is full of attraction due to the low cost, high sensitivity and good selectivity [13,14]. According to fabrication materials, electrochemical sensors can be divided into enzyme-based and non-enzymatic sensors. Compared with enzyme-based sensor, non-enzymatic sensor exhibits various advantages such as wide range of application, simple fabrication and storage condition [13,14]. However, enzyme-based sensor always exhibits higher sensitivity and better selectivity. Therefore, how to improve the integrated performance of electrochemical sensor has attracted much attention.

Nowadays, the rapid development of nanotechnology provides an exciting opportunity for improvement of electrochemical sensors. Various nanostructures such as nanometal, nanometallic oxides, nanocarbon materials and DNA nanostructures have been used for fabrication of electrochemical sensors due to their extra large surface area, high surface concentrations of edges, corners, defect sites, and other unusual structural features [15–19]. In addition, in order to make up for the shortage of single materials such as the poor conductivity, general catalytic activity or aggregation in synthetic step, electrochemical sensors based on composite materials such as metal/metal, metal/metallic oxides, metal/carbon material and DNA structure/nanomaterials have been selected the most in recent years due to the cooperation between different materials [20–24]. Zhang et al. [21]. constructed an amperometric biosensor based on graphene-platinum (RGO-Pt) nanocomposites to measure the release of H_2O_2 from living PC-12 cells. RGO provided a platform for growth of Pt nanoparticles without aggregation

* Corresponding author.
E-mail addresses: qinglinsheng@126.com (Q. Sheng), zhengjb@nwu.edu.cn (J. Zheng).

http://dx.doi.org/10.1016/j.snb.2016.11.125
0925-4005/© 2016 Elsevier B.V. All rights reserved.



Scheme 1. Schematic Illustration for the detection of H_2O_2 released from live cells.

and Pt particles acted as catalyst toward reduction of H_2O_2. The sensor exhibited low detection limit, high sensitivity and wide linear range which was for H_2O_2 detection in living cells. Li et al. [22]. constructed a microfluidic paper-based analytical device (μ-PAD) for synchronous sensitive and visual detection of H_2O_2 released from MCF-7 cells based on an in situ hydroxyl radicals cleaving DNA approach. The μ-PAD was constructed by concanavalin A, graphene quantum dots (GQDs) labeled Au@Pd alloy nanoparticles (NPs) probe, and MCF-7 cells on the surface of the vertically aligned bamboo like ZnO. Shim et al. [23]. prepared a kind of dealloyed-AuNi dendrite anchored on carboxylic acid groups of a conducting polymer for detection of H_2O_2 released from cancer cell A549 and normal cell. The dendrite formation is initiated on a poly (benzoic acid-2,2′:5′,2″-terthiophene) (pTBA) layer, where the polymer layer acts as a stable substrate to improve the long-term stability and catalytic activity of the alloy electrode. The modified electrode exhibits an extra low detection limit of 5 nM. According to what mentioned above, composite materials have been used widely for construction of electrochemical sensors due to the satisfied cooperation between every single materials which exhibit extra properties such as stability, conductivity, catalytic activity, etc [24]. However, the complex fabrication step and mechanism of action are always the shortage of composites based sensors. In order to obtain the satisfied modified electrode, researchers have to find the proper substrates and catalysts. In addition, the complex cooperation mechanism between the composites is always a confused question. Therefore, how to improve the integrated performance of singular materials based electrochemical sensors is one of the most urgent issues to be solved.

As previous reports, active or reactive crystalline facet of material plays a lead role in its catalytic application [35]. Therefore, modification of crystalline facet of nanomaterial may provide an opportunity for singular material based electrochemical analysis. Manganese dioxide (MnO_2), one of transition metal oxides, has attracted much attention due to low cost, environmental friendliness, high theoretical capacitance and catalytic property [25–28]. As one of the most used metal oxides in recent years, on one hand, MnO_2 has been used commonly in fabrication of electrochemical H_2O_2 sensors due to the simple synthetic methods and acceptable catalysis towards H_2O_2. On the other hand, due to the poor conductivity and unattractive catalytic property, it often has to be used as substrates to provide platform for fabrication of composite materials [29–32]. However, the situation will be changed. In this work, we report a novel and simple sensing platform based on acidification of MnO_2 for detection the release of H_2O_2 from living cells (Scheme 1). Flower-like MnO_2 (f-MnO_2) was synthesized first. Then f-MnO_2 was acidized by the mixture of sulfuric acid and nitric acid to modify its crystalline facets. Compared with the normal composite materials, the obtained acidized MnO_2 (a-MnO_2) exhibits the following advantages: easier synthetic procedure, better catalytic properties and lower charge transfer resistance. At last, the a-MnO_2 was dropped on surface of glassy carbon electrode (GCE) to fabricate electrochemical detection platform. Considering the low detection limit, wide linear range and fast response time, the platform was applied to measure release of H_2O_2 from living cells (PC-12 rat adrenal medulla pheochromocytoma and normal adrenal medulla cells) successfully.

2. Experimental

2.1. Preparation of MnO_2, a-MnO_2 and modified electrode

The preparation method of MnO_2 has been used in our previous work [33]. 50 mg MnO_2 were dissolved in mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v ratio) in ultrasonic bath. Then the mixture was performed on magnetic stirring for 4 h to obtain. After centrifugation, washing and drying, a-MnO_2 was obtained. The preparation method of modified electrode has been used in our previous work [24]. 1 mg a-MnO_2 nanomaterials were dispersed in chitosan (1 mL, 0.05%) solution under ultrasound. Then 10 μL suspension was dropped on surface of GCE. The modified electrode can be expressed as a-MnO_2/GCE.

2.2. Electrochemical detection of H_2O_2 released by cells

Electrochemical detection of H_2O_2 released by cells was realized by amperometric method. PC-12 rat adrenal medulla pheochromocytoma and normal adrenal medulla cells were used in this research. The cells were suspended in PBS (0.1 M) and 1 μM AA was injected to the cells suspension every times to motivate cells generate H_2O_2. The electrochemical experiments were conducted in water bath under 37 °C.

Detailed materials, characterizations and experimental steps were provided in supplementary information.

3. Results and discussions

3.1. Physicochemical characterization

Fig. 1A–C show the SEM (A, B) and TEM (C) images of MnO_2. Similar as our previous reports [33], the obtained MnO_2 exhibits flower-like structure which is composed by wrinkle-like nanolayer. The diameter of single flower-like structure is about 800 nm and the monolayer is extra thin. However, the morphology is changed a lot after acidification. Fig. 1D–F show the SEM (D, E) and TEM (F) images of a-MnO_2. It can be seen that the original flower-like structure is broken instead by large amounts of broken pieces. This may be due to the following reasons. In this research, concentrated acid (concentrated H_2SO_4 and HNO_3) was used to acidize MnO_2. Concentrated H_2SO_4 will react with MnO_2 under high temperature. Although the reaction was performed under room temperature, the reaction will be processed slowly and the flower-like structure of MnO_2 will be corroded.

Fig. 1G shows the FTIR spectra of materials (a for MnO_2 and b for a-MnO_2). The band at 750 cm^{-1} in Fig. 1G a can be due to the Mn–O stretching vibrations which may be caused by manganese oxide lattice (MnO_6 octahedral). The 3500 cm^{-1} band can be attributed to the hydroxide group and two peaks at 1400 and 1698 cm^{-1} are due to H—O—H. Compared with Fig. 1G a, G b shows similar spectra. The only differences are the band at 3400 cm^{-1} with extra intensity and the band at 1698 cm^{-1} with weak intensity. This may be due to the sufficient hydroxide groups caused by acidification of MnO_2 and dehydration of MnO_2 caused by concentrated acid. XRD

Download English Version:

https://daneshyari.com/en/article/5009736

Download Persian Version:

https://daneshyari.com/article/5009736

Daneshyari.com