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Ultrasensitive electrochemical detection of H_2O_2 in living cells based on ultrathin MnO_2 nanosheets

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ABSTRACT

Using a facile and efficient method, two-dimensional (2D) ultra-thin MnO_2 nanosheets were successfully prepared. Due to the large specific surface area and mesoporous structure, MnO_2 nanosheet is a good candidate for use as an enhanced electrochemical sensing material. MnO_2 nanosheets were immobilized onto glassy carbon electrodes with Nafion film to construct a H_2O_2 electrochemical nonenzymatic sensor. Amperometric study showed MnO_2 nanosheets exhibited very high electrocatalytic activity towards H_2O_2 reduction. A very low detection limit (5 nM) was reached with a wide linear range (25 nM–2 μM and 10–454 μM) and a high sensitivity of 3261 mA M^{-1} cm^{-2}. The fabricated H_2O_2 sensor also exhibited excellent selectivity, good reproducibility and long-time stability. Furthermore, the constructed high sensitive sensor was successfully applied to perform real-time monitoring trace concentration of H_2O_2 released by SP2/0 cells, indicating that MnO_2 nanosheets provide a new platform for developing high performance electrochemical sensors in biological applications.

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1. Introduction

H_2O_2, produced by disproportionation of unstable reactive oxygen species (ROS) superoxide ions, plays an important role in intracellular signaling pathways of healthy cell [1,2]. Excessive amount of H_2O_2 could cause a variety of biological damages, giving rise to progressive neurodegenerative diseases as well as cancer, such as Alzheimer disease, Parkinson's disease and etc [3,4]. In order to better understand the biological effects of H_2O_2 and find new therapeutic strategies for diseases, it is of great importance to perform real-time detection of intracellular H_2O_2. Various methods such as fluorescence [5,6], colorimetry [7,8], chemiluminescence [9,10], and electrochemical methods [11–14] have been developed for H_2O_2 detection. Among these methods, the electrochemical technique have considered to be an efficient method for H_2O_2 detection owing to its high sensitivity, good selectivity and simple operation. Our group recently used MoS_2-Au hybrids to construct a sensitive H_2O_2 electrochemical biosensor for determination of H_2O_2 released from living cells [15]. Compared with enzyme-based electrochemical biosensors, nonenzymatic electrochemical sensors have received much more attention in practical applications because enzyme can easily lose their biological activity caused by denaturation [16–20]. Many nonenzymatic electrochemical sensors have been developed for real-time monitoring of H_2O_2 from living cells in recent years [17–20].

Two-dimensional (2D) layered materials such as monolayer graphene [21,22] and layered transition metal dichalcogenides (MoS_2, WS_2, etc) [23,24] attracted a great deal of attention over the last decade. With the advantage of abundant exposed surface active sites and exceptionally large specific surface area, such layered nanosheets display high catalytic performance and are widely applied in the fields of batteries [24–26], supercapacitors [22,27], sensors[28–31] and etc.

Recently, transition-metal oxides, such as Fe_3O_4, Co_3O_4, SnO_2, *etc* also have been employed as advanced nanomaterials in electrochemical biosensing, energy conversion and storage owing to their intrinsic advantages, such as large specific surface area, high electrocatalytic activity, diverse morphology and low cost of raw materials [32–36]. Manganese dioxide (MnO_2), as a type of transition metal oxide, has received much more attention for its role as an electrode material for sensors, batteries and supercapacitors attribute to its good electrochemical performance in neutral electrolyte, high theoretical capacity and nontoxicity [37–41].

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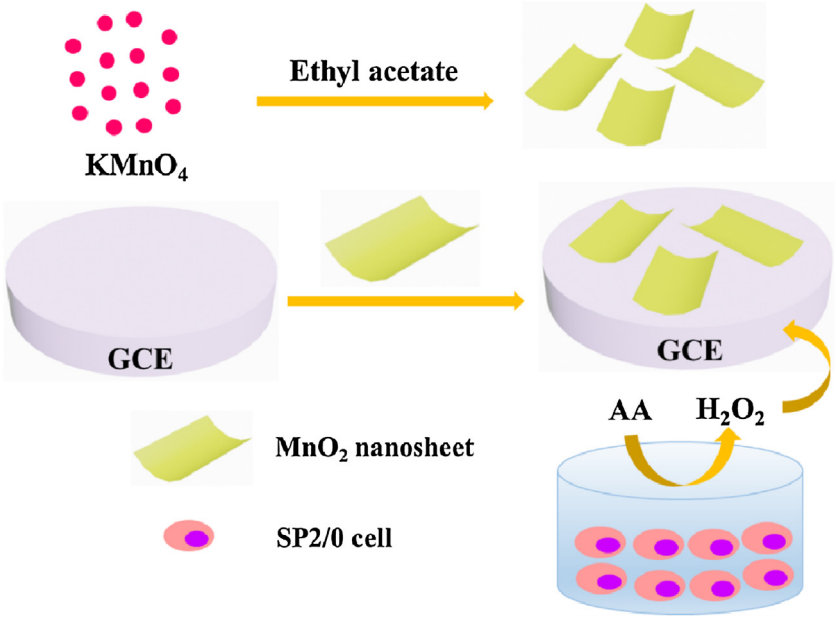

Scheme 1. Schematic of the Synthesis Procedure of MnO_2 Nanosheets and the MnO_2 Nanosheets Modified GCE Used for Detecting H_2O_2 Released from SP2/0 Cells Stimulated with Ascorbic Acid (AA).

MnO_2 and different carbon materials (graphene, carbon nanotubes, carbon foam and etc.), metals or metal oxides were formed composites/hybrids and were widely used as electrode materials for detection of hydrogen peroxide [37,42,43], glucose [38], mercuric chloride [44], and etc. However, in order to measure the trace concentration of H_2O_2 released by living cells/organisms, there is an urgent need to develop a much more sensitive electrochemical sensor which based on a desirable nanomaterial with unique electrocatalytic activity.

Inspired by this, in this work, a H_2O_2 electrochemical nonenzymatic sensor is constructed based on MnO_2 nanosheets to monitor H_2O_2 released by living cells (Scheme 1). A facile and efficient method is reported to synthesize ultrathin MnO_2 nanosheets. Then MnO_2 nanosheets have been used as the modifying layer on the surface of the glass carbon electrode (GCE) to construct a H_2O_2 electrochemical nonenzymatic sensor. The amperometric study shows that nano-molar H_2O_2 can be detected within our sensor. Furthermore, the sensor also shows high selectivity and good stability toward H_2O_2 detection. The high electrocatalytic activity of MnO_2 nanosheets might be due to its high specific surface area and porous structure. Owing to its excellent electrochemical performance, the constructed sensor was successfully applied to perform real-time monitoring trace concentration of H_2O_2 released by living cells with satisfactory results, indicating the MnO_2 nanosheets provide a promising platform as a good electrochemical sensing material in practical applications.

2. Experimental section

2.1. Reagents and apparatus

Phosphate buffer solution (PBS, 0.1 M, pH 7.0) comprising NaH_2PO_4 and Na_2HPO_4 was used as the supporting electrolyte. 1 × PBS (pH 7.4) including Na_2HPO_4 (10.14 mM), KH_2PO_4 (1.76 mM), KCl (2.68 mM) and NaCl (136.75 mM) was utilized to wash and disperse SP2/0 cells. Nafion solution was purchased from DuPont. All other reagents were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd., Double distilled water was used throughout the experiments.

2.2. Synthesis of MnO_2 nanosheets

MnO_2 Nanosheets were prepared by the reported work [45]. 150 mL $KMnO_4$ (0.02 M) solution was mixed with 40 mL ethyl acetate to form a mixture, and was heated to reflux at 85 °C until the color of the mixture was faded. Colloidal product was separated by a separating funnel. Dark brown solution in the down layer was obtained and washed with double distilled water and ethanol for three times, individually. At last the products were dried in air at 50 °C.

2.3. Fabrication of modified eelectrode

GCE with a diameter of 3 mm was polished with Al_2O_3 slurry (0.3 μm), later cleaned by ultrasonication with ethanol and water respectively. Then a 5 μL of the 10 mg/mL MnO_2 nanosheets which was suspended in 1% Nafion solution was added onto the GCE surface and dried in air as a working electrode.

2.4. Materials characterization and electrochemical tests

The morphology of nanomaterials was observed on field-emission scanning electron microscopy (FESEM, Supra 55, Zeiss) and transmission electron microscopy (TEM, JEM-2100). High resolution transmission electron microscopy images, scanning transmission electron microscopy (STEM) images and EDS mapping were captured on the Tecnai G^2 F30 transmission electron microscopy at an acceleration voltage of 300 kV. XRD characterization was carried out on Bruker AXS D8 Advance diffractometer. Raman spectra were collected with a Confocal Raman spectrometer (In Via, Renishaw Co.). X-ray photoelectron spectroscopy (XPS) analysis was performed on Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. Atomic force microscope (AFM) images were obtained with a MFP-3D-SA (Asylum Research, USA). The specific surface area and pore size distribution were obtained from the N_2 adsorption–desorption isotherms at high pressure gas adsorption instrument (Setaram, PCT ProEvo).

Electrochemical tests were carried out by a CHI760D electrochemical workstation (CHI Co., Shanghai) with a three-electrode

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