Non-enzymatic electrochemical sensing of hydrogen peroxide based on polypyrrole/platinum nanocomposites

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A B S T R A C T

In this work, we report a facile strategy for the preparation of polypyrrole/platinum nanocomposite (PPy/Pt nanocomposite), namely small and surface-clean Pt nanoparticles (Pt NPs) densely dispersed on polypyrrole nanoparticles (PPy NPs) by a simple, ultrafast, and microwave-assisted polyol process. The as-made nanocomposite was demonstrated to possess a good electrocatalytic activity toward the reduction of H_2O_2 by obviously enhancing the detection sensitivity and decreasing H_2O_2 reduction overpotential at −0.175 V (vs. Ag/AgCl). Accordingly, a selective, stable, repeatable and reproducible non-enzymatic electrochemical sensor of H_2O_2 based on the nanocomposite was constructed.

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1. Introduction

Hydrogen peroxide (H_2O_2), is not only a common chemical used widely in the agriculture, food processing, medical treatment and chemical industry, but also an important small molecule generated in a wide range of oxidative biological reactions and related to the different kinds of disorder in human body, such as cancer, heart attack, Alzheimer's, Parkinson's, etc. [1–3]. Thus, the rapid, sensitive and selective detection of H_2O_2 is of practical significance. So far, various kinds of analytical techniques have been applied for the quantitative detection of H_2O_2, including titration, spectrophotometry, chemiluminescence, fluorescence, cell imaging, electrochemical method, etc. [4–13]. Compared with other techniques, the electrochemical methods stand out due to their intrinsic merits, such as simplicity, low costs, low detection limit and fast response for analysis [8–13]. For electrochemical detection of H_2O_2, enzyme-based biosensors, like the most widely used horseradish peroxidase (HRP) [12,13], have been under considerable attention. However, those HRP-based electrochemical sensors of H_2O_2 are greatly restricted by some inherent disadvantages, like poor reproducibility, chemical and thermal instabilities and critical operating condition, which hinder the practical applications [12,13]. In order to overcome those obstacles, increasing studies have focused on constructing non-enzymatic electrochemical H_2O_2 sensors based on functional nanocomposites which have several advantages including easy handling, high stability, fast response, etc. [8–11].

Organic conducting polymers with various compositions and nanostructures have witnessed a wide range of potential application in electrochemical sensors and electrocatalysis over the past few decades [14,15]. As one of the most important conducting polymers, polypyrrole (PPy) with different nanostructures involving membrane, nanoring, nanofibers [16–18], nanotubes [19] and nanoparticles [20], has been widely used for electrochemical detection of various substances due to its intrinsic physical and chemical properties such as effectively loading metal nanomaterial, high electronic conductivity and good environmental stability. Recently, a wide variety of functional nanocomposites based on PPy nanomaterial have been prepared and applied to non-enzymatically detect H_2O_2. However, those methods to fabricate PPy-based nanocomposites suffered from such disadvantages as tedious steps, high cost and time-consuming processes [21,22]. And there was still a wide research field to be improved on the corresponding analytical performances obtained based on PPy nanomaterials [16–22]. For instance, the detection sensitivity was not high enough to precisely quantitate the change of H_2O_2 concentration. Moreover, the detection overpotential was still too high to avoid interferences caused by common electroactive species during the measurement. Therefore, it is highly desirable to develop a simple and rapid method to prepare PPy-based nanocomposite to remarkably increase the sensitivity and obviously lower the overpotential of the electrochemical determination of H_2O_2.

Noble metal nanomaterials have attracted extensive attention owing to their extraordinary catalytical activities [23–28].

Particularly, metallic Pt nanoparticles (Pt NPs) exhibited superior electrocatalytical activity toward the oxidation of formic acid [23], alcohol and glucose [9], and reduction of oxygen [24,25]. In addition, Pt NPs have been demonstrated to lower the overpotential and improve the sensitivity of the H_2O_2 reduction [21,22]. Therefore, one can image that the elaborate combination of Pt NPs with the PPy nanomaterial will improve the integrated analytical performance of the PPy-based nanocomposite for non-enzymatic electrochemical detection of H_2O_2.

Herein, PPy/Pt nanocomposite was fabricated simply by direct deposition of Pt NPs on PPy NPs through an ultrafast microwave-assisted polyol process. The as-prepared PPy/Pt nanocomposite was used to construct non-enzymatic electrochemical H_2O_2 sensor, which possessed superiority such as stability, selectivity, repeatability, reproducibility, particularly high sensitivity. Furthermore, the proposed sensor was successfully applied to detect H_2O_2 in commercial gargles samples.

2. Experimental

2.1. Chemicals

Hydrogen peroxide (H_2O_2, 30 wt%), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), potassium hexachloroplatinate (IV) (K_2PtCl_6, 99%), uric acid (UA, 99%) and D-(+)-glucose (Glu, 99%) were purchased from Alfa Aesar (Tianjin, China). Pyrrole monomer (Py, 98%), ethylene glycol (EG, 99.8%) and poly(vinyl alcohol) (PVA, Mr ∼ 31,000) were purchased from Sigma–Aldrich (Shanghai, China). Citric acid (CA, 99%), NaH_2PO_4 (99.9%), Na_2HPO_4 (99.9%) and KCl (99.9%) were purchased from Beijing Chemical Reagents Company (Beijing, China). All the reagents were of analytical grade and used as without further purification. Ultrahigh-pure N_2 (99.999%) was used for deaeration. A fresh solution of H_2O_2 was prepared just before use. All aqueous solutions were prepared with double distilled water.

2.2. Apparatus

In all the procedures, the water used was purified through an Olst ultrapure K8 apparatus (Olst, Ltd., resistivity >18 MΩ). Transmission electron microscopy (TEM) was performed with a JEOL-100CX electron microscope under 80 kV accelerating voltage. High-resolution transmission electron microscopy (HRTEM) images were taken from a JEOL Model JEM-2100F TEM at 200 kV. Scanning electron microscopy (SEM) images were determined with a Hitachi SU8010 SEM. X-ray photoelectron spectroscopy (XPS) was conducted using an Escalab 250 X-ray Photoelectron Spectroscope (Thermofisher, American) employing a monochromatic Al Kα radiation. Microwave-assisted synthesis of PPy/Pt nanocomposite was carried out in a microwave machine (CEM Matthews. NC, USA) using single mode and continuous power at 2.45 GHz. All the electrochemical measurements were carried out at room temperature under nitrogen atmosphere on CHI-842C electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A three-electrode system was used in the experiment with a glassy carbon electrode (GCE, geometric area = 0.0707 cm^2) as the working electrode, an Ag/AgCl electrode (saturated KCl) as reference electrode and a Pt wire electrode as counter-electrode, respectively.

2.3. Synthesis of PPy NPs

Formation of PPy NPs was performed using modified literature methods [29]. A typical synthesis was conducted as follows, 1.5 g PVA was dissolved completely in 20 mL double-distilled water at room temperature, followed by adding 1.24 g $FeCl_3 \cdot 6H_2O$ (s).

After 1 h to allow equilibration, 142 μL pyrrole monomer was introduced into the aqueous PVA/$FeCl_3$ solution. Polymerization proceeded while stirring for 4 h. After completion of polymerization, the resulting nanoparticles were separated from the dispersion solution by centrifugation and washed several times with hot water to remove impurities. The obtained PPy NP precipitate was redispersed in 1 mL double-distilled water for further use.

2.4. Synthesis of PPy/Pt nanocomposite

In a typical experiment, the nanocomposite synthesized by the following process: 100 μL as-prepared PPy NPs suspension, 1.154 mL pure water, 1.330 mL EG, 95 μL K_2PtCl_6 (10 mM) was successively added into a vial followed by vortex mixing for several minutes to get a homogeneous dispersion. Subsequently, the resultant dispersion was transferred into a microwave reaction vessel and placed in the vessel holder. The desired temperature and time were programmed by the intelligent software before the reaction triggered. The maximum power setting was set as 250 W and the pressure limit was 250 psi. The temperature and reaction time were set as 120 °C and 10 min, respectively. After the reaction completed, microwave reaction vessel was allowed to cool down to room temperature. The as-made PPy/Pt nanocomposite was collected by centrifugation and washed with deionized water and ethanol for three times and redispersed in 1 mL pure water for further electrochemical test.

2.5. Electrode preparation

Prior to the modification, the glass carbon electrode was polished completely with 1.0, 0.3, and 0.05 μm alumina slurry, respectively, and sonicated successively in 1:1 nitric acid, absolute alcohol, and double-distilled water. The cleaned electrode was dried with high-purity nitrogen steam. PPy/Pt nanocomposites-modified GCE (PPy/Pt/GCE) was prepared by casting 20 μL of the PPy/Pt suspension on the GCE surface and dried with an infrared lamp. For comparison, the PPy NPs-modified GCE (PPy/GCE) was prepared in the same way. The PBS (0.1 M, pH 7.0) were deoxygenated with nitrogen and kept under nitrogen atmosphere during electrochemical studies.

3. Results and discussion

3.1. Characterization of the PPy/Pt nanocomposite

It can be seen from Fig. 1A that the PPy NPs is approximately spherical with an average diameter of ca. 55 nm. As was depicted in Fig. 1B and C, a mass of tiny Pt NPs were successfully prepared and densely loaded on PPy NPs. Fig. 1C showed that the average size of the small Pt nanoparticle was ca. 3 nm and the dominant lattice distance was ca. 0.23 nm in Fig. 1D inset, consistent well with the d_{111} interplanar distance (0.23 nm) of face-centered-cubic (fcc) crystalline Pt, which suggested that the surface of the small Pt nanoparticle was predominated by exposed Pt (1 1 1) facets [30,31].

The compositions of the produced PPy nanoparticle and PPy/Pt nanocomposite were then characterized by X-ray photoelectron spectroscopy (XPS). Fig. 2A displayed the survey spectra of PPy/Pt nanocomposite and PPy NPs, respectively. In both spectra, there were three predominant peaks at 284.7, 400.0 and 531.6 eV, corresponding to the C_{1s}, N_{1s}, and O_{1s}, respectively [32]. Compared to the spectrum of PPy NPs, four extra peaks centered at around 71.4, 101.0, 316.0 and 333.0 eV can be obviously observed in the spectrum of PPy/Pt nanocomposite, corresponding to the binding energies of Pt 4f, Pt 5s, Pt $4d^5$ and Pt $4d^3$ [33]. The high-resolution