Electrochimica Acta 176 (2015) 497–503

Contents lists available at ScienceDirect

Electrochimica Acta

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

Efficient and rapid microwave-assisted route to synthesize Pt–MnO_x hydrogen peroxide sensor

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ARTICLE INFO

Article history:
Received 11 May 2015
Received in revised form 18 June 2015
Accepted 30 June 2015
Available online 3 July 2015

Keywords:
Platinum nanoparticles
hydrogen peroxide sensor
MnO_x

ABSTRACT

A novel electrochemical sensor for the detection of hydrogen peroxide (H_2O_2) is proposed based on carbon supported Pt-MnO_x and Pt nanoparticles, successfully synthesized via microwave irradiation polyol method. The physicochemical properties of the Pt-MnO_x and Pt nanoparticles were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Transmission electron microscopy (TEM). Electrochemical properties of the nanoparticles were investigated by cyclic voltammetry (CV) and chronoamperometry (CA). Electrochemical measurements indicate that the oxidation current of H_2O_2 is linear (R^2=0.998) to its concentration from 2 μM to 4.0 mM with a detection limit of 0.7 μM (signal/noise = 3). In addition, Pt-MnO_x is not affected by ascorbic acid (AA) and uric acid (UA) which are common interfering species. Meanwhile, this Pt-MnO_x non-enzymatic H_2O_2 sensor exhibits excellent selectivity, stability and reproducibility. Thus, this novel non-enzymatic sensor can be found practical applications in H_2O_2 detection.

1. Introduction

The accurate determination of hydrogen peroxide (H_2O_2) has a great importance because it is a by-product of several important oxidases and significant mediator in chemical, biological, food, and environmental processes [1–3]. Titrimetry, fluorometry, spectrophotometry, and electrochemistry are the most commonly used methods to detect H_2O_2 [4–6]. Particularly, the electrochemical techniques based on enzyme-modified electrodes have attracted considerable interest. However, these electrodes have some drawbacks such as instability, high cost of enzymes, and complicated immobilization procedures. To overcome these drawbacks, Pt nanoparticles can be used for construction of non-enzymatic sensors to improve the electrocatalytic activities towards H_2O_2 [7–9]. Nevertheless, these Pt based non-enzymatic sensors have high cost and low sensitivity due to surface poisoning by the adsorbed intermediates [10]. Therefore, the fabrication of non-enzymatic H_2O_2 sensors having a low cost with higher activity compared to Pt alone has gained importance. In this respect, Pt-based nanoparticles such as metal and metal oxides could be employed as non-enzymatic H_2O_2 sensors due to the improved mechanical and electronic properties of Pt [11,12].

Metal oxides are advantageous due to their high electron communication features and chemical stability. They can be combined with a conducting support to promote electron transfer and provide a remarkable synergistic effect because unsupported metal oxide catalysts have very low surface areas, decreasing the sensing activity. With these purposes, several metal oxides such as ZnO, CuO, Co_3O_4, MnO_2 have been used for the fabrication of sensors [13–18]. Among all the metal oxides, MnO_2 is an attractive inorganic material because of its low cost and high catalytic ability towards H_2O_2. However, MnO_2 has poor electrical conductivity and thus become less sensitive in electrochemical analysis. Therefore, MnO_2 has to be modified to increase the conductivity. Various MnO_2 nanomaterials with different synthesized methods have been developed for the construction of sensors [19–22].

Shape and size greatly affect the characteristics of metal nanoparticles. Hence, it is important to develop effective methods for the preparation of nanoparticles with well-controlled shape and size. The currently used methods include electrodeposition [23], redox reaction [24], thermal decomposition [25], hydrothermal method [26]. Microwave assisted polyol is a novel technique for preparing nanosized inorganic particles. The enhanced reaction kinetics, formation of novel phases and morphologies, obtaining better and smaller size, energy saving during the synthesis are the main advantages of the microwave synthesis route. Although many studies were devoted to microwave synthesis method, microwave assisted preparation of MnO_x modified carbon

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http://dx.doi.org/10.1016/j.electacta.2015.06.151
0013-4686/

supported Pt (Pt-MnO_x@C) and its application of as a H_2O_2 sensor have not been studied before.

In this work, Pt-MnOx@C and Pt@C catalysts were prepared by microwave assisted polyol method. The electrocatalytic performances of the synthesized catalysts were evaluated by H_2O_2 oxidation.

2. Experimental

2.1. Reagents and Instruments

Carbon powders were of spectroscopic purity and were purchased from Aldrich. $H_2PtCl_6.6H_2O$ (38-40% Pt) and $MnCl_2$ metal salts were obtained from Sigma. 0.1 M phosphate buffer solution (pH 7.5) was prepared from 0.1 M Na_2PO_4 and NaH_2PO_4 in ultrapure water. H_2O_2 solution (30%) was purchased from Sigma and a fresh solution of H_2O_2 was prepared daily. Other reagents were of analytical grade and used as received. Aqueous solutions were prepared with distilled water from a Millipore system. All the chemicals were used as supplied without purification.

2.2. Synthesis and preparation of Pt-MnO_x@C and Pt@C electrodes

Pt-MnO_x@C and Pt@C catalysts were prepared by microwave assisted polyol method. For the preparation of Pt@C catalysts, 0.051 g of $H_2PtCl_6.6H_2O$ (38-40% Pt) metal salt and 0.1 g of carbon support was dispersed in ethylene glycol and glycerol mixture ($V_{ethylene\,glycol}/V_{glycerol}$=90/10). In order to deposit Pt on carbon support, 5 mL 0.12 M KBr and 5 mL 0.05 M NaOH were added drop by drop under magnetic stirring to this mixture. After the resulting mixture was treated in ultrasonic bath during 1 h, microwave reactor tubes containing the resulting solution was put into a Microwave reactor (Anton Paar monowave 300) and heated for 2 min at 130 °C. Finally, the samples were filtered, washed with distilled water and ethanol, and dried in a vacuum oven at 60 °C. Pt metal loading per gram carbon was 20% for Pt@C catalyst. Pt-MnO_x@C catalyst was also prepared by microwave assisted polyol method at Pt.: Mn (05:05) atomic ratio. For the preparation of Pt-MnO_x@C catalyst, 0.051 g of $H_2PtCl_6.6H_2O$ (38-40% Pt) metal salt and 0.013 g of $MnCl_2$, and 0.1 g of carbon support dispersed in ethylene glycol and glycerol mixture ($V_{ethylene\,glycol}/V_{glycerol}$=90/10), 5 mL of 0.12 M KBr and 5 mL of 0.05 M NaOH were added. Then, this mixture was heated in microwave reactor for 2 min at 130 °C. Next, sample was filtered, washed with distilled water and ethanol, and dried in a vacuum oven. Pt metal loading per gram carbon was also fixed as 20% for Pt-MnO_x@C catalyst.

2.3. Preparation of Sensor

The working electrode was prepared with a following procedure. A glassy carbon electrode (GCE, d= 3 mm) was polished with 1micron, 0.3 micron, and 0.05 micron alumina slurry. Then, it was cleaned thoroughly with double-distilled water and ethanol and then allowed to dry at room temperature. For the electrode preparation, 5 mg catalyst was dispersed in 1 mL 0.5% Nafion® solution (mixture of Aldrich 5% Nafion solution and ethanol). To modify the GCE surface, 3 μL of this ink was spread on the surface of GCE and dried at room temperature to remove the solvent.

2.4. Apparatus and characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded between $2\theta = 10.0–85.0°$ with 0.05° intervals on a Bruker D 8 Advance X-ray diffractometer using Cu-Kα (λ = 1.5405 A°) as a radiation source. Surface information of Pt-MnO_x@C and Pt@C catalysts was recorded by X-ray photoelectron spectroscopy (XPS, SPECS) using X-ray tube working at 15 kV and 350 W with Mg-Kα (hv = 1253.6 eV) unmonochromatized radiation.

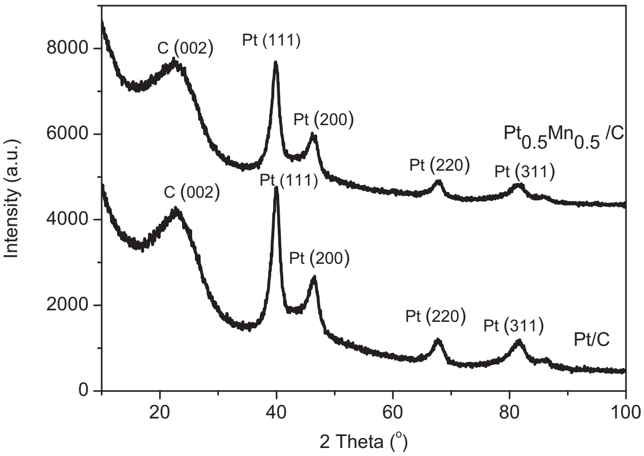

Fig. 1. XRD patterns of Pt-MnO_x@C and Pt@C catalysts.

The charging effects were corrected by using the C 1s peak, as reference for all samples at a binding energy (BE) of 284.5 eV. The morphologies of the Pt-MnO_x@C and Pt@C catalysts were characterized by a transmission electron microscope (TEM). The particle size of the catalysts was predicted by assuming spherical particles.

Electrochemical characterization was performed on a CHI 660E electrochemical workstation. All experiments were conducted in a three-electrode system at room temperature with Pt wire as a counter electrode and Ag/AgCl (sat. KCl) as a reference electrode. Cyclic voltammetry (CV) and chronoamperometry (CA) techniques were performed on Pt-MnO_x@C and Pt@C catalysts. Cyclic voltammograms and chronoamperomograms were recorded in 0.1 M phosphate buffer solution as the supporting electrolyte on these catalysts. During the experiments, ultrahigh purity Ar was introduced into the electrochemical cell above solution as a protection atmosphere. First of all, CV measurements were taken in 0.1 M phosphate buffer solution with a scan rate of 50 mV s^{-1} on Pt-MnO_x@C and Pt@C electrodes. Then, the subsequent addition of H_2O_2 solution was performed in 0.1 M phosphate buffer solution with a scan rate of 50 mV s^{-1}.

Amperometric measurements were executed in a 0.1 M phosphate buffer solution under stirred condition and the

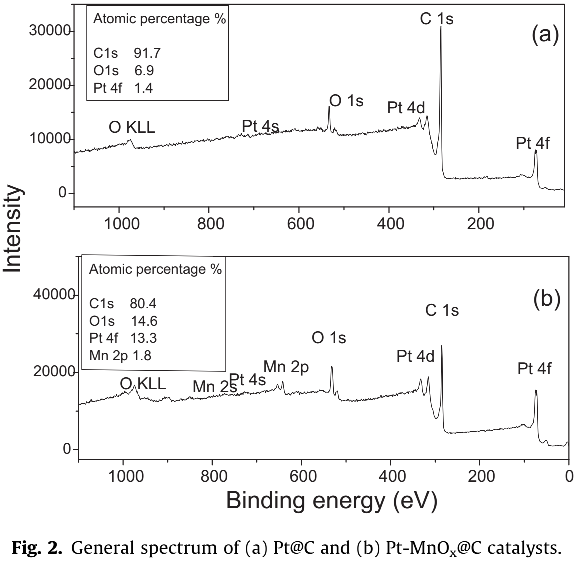

Fig. 2. General spectrum of (a) Pt@C and (b) Pt-MnO_x@C catalysts.