Sensors and Actuators B 196 (2014) 398–405

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Electrochemical determination of hydrogen peroxide using copper/porous silicon based non-enzymatic sensor

Ali A. Ensafi*, M. Mokhtari Abarghoui, B. Rezaei

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 18 January 2014
Accepted 5 February 2014
Available online 15 February 2014

Keywords:
Porous silicon based nanocomposite
Hydrogen peroxide detection
Non-enzymatic sensor
Amperometry

ABSTRACT

Copper on porous silicon (Cu/PSi) nanocomposite powder is a new electrode material synthesized by electrodeless deposition of copper nanoparticles on the etched PSi powder in a solution containing hydrofluoric acid and $CuSO_4$. The nanocomposite is selective for electrochemical hydrogen peroxide (H_2O_2) reduction and shows a wide linear range (0.50–3.78 mmol L^{-1}), low detection limit (0.27 μmol L^{-1}), fast response (less than 5 s), good signal reproducibility (R.S.D. = 1.5%), long-term stability (more than one month), plus the low cost. No interference was observed from common species such as ascorbic acid, dopamine, uric acid and glucose.

1. Introduction

Although porous silicon (PSi) was first discovered accidentally by Uhlir [1] in 1956, significant interest in this material exploded in the early 1990s when Canham discovered photoluminescence of porous silicon [2]. The unique physical and chemical properties of PSi such as biocompatibility and biodegradability, high tunable porosity, high surface area and photonic and photoluminescence properties make this material popular in the fields of tissue engineering, molecular-sensing, drug delivery and bio-sensing [3–6]. In addition, PSi surfaces show other interesting features by modification with readily available chemicals such as silanes at mild reaction conditions for different applications [7–10]. It is surprising that very little research has been made in the field of electrochemical sensors based on porous silicon even if electrochemical sensors have several important advantages such as easy preparation, low cost, high sensitivity and simplicity. In addition, this type of sensors can be miniaturized more easily than optical sensors.

Fast and easy determination of H_2O_2 has attracted much attention due to its important role in biology, industry, food, pharmaceutical and environmental researches [11,12]. Several methods such as titrimetry, spectrophotometry, chromatography, chemiluminescence, colorimetry and electrochemistry are available for determination of H_2O_2 [13–16]. Among these analytical methods, electrochemical sensors are attractive choice, due to their simplicity, practicality and low-cost [17–19]. Enzymatic electrochemical sensors based on immobilization of enzymes such a myoglobin [20], horseradish peroxidase [21] and hemoglobin [22] are used for selective and sensitive analysis of H_2O_2. On the other hand poor reproducibility, chemical and thermal instabilities and complicated immobilization procedures of these sensors [23,24] have turned recent efforts to direct determination of H_2O_2 at enzyme free sensors [18,19].

In this work for fabricating a new electrochemical sensor based on PSi, Cu/PSi nanocomposite is synthesized by chemical etching of silicon microparticles followed by electrodeless deposition of copper nanoparticles on the etched silicon. Then, it is used for fabricating of Cu/PSi nanocomposite based carbon paste electrode (CPE). It has been found that this electrode has good electrocatalytic activity on the reduction of H_2O_2 in phosphate buffer solution (PBS) at pH 7.0. The detection limit and linear dynamic range of the modified electrode with Cu/PSi nanocomposite are comparable to, and even better than those recently obtained by other works [19,25–32]. Comparisons of the results from the different studies are shown in Table 1.

2. Experimental

2.1. Chemicals

Si powder (mean particle size of 40 μm) was purchased from Sigma–Aldrich (St. Louis, USA). Graphite, nujol, nitric acid, hydrofluoric acid, sodium nitrate, hydrogen peroxide, sodium nitrite and glucose were purchased from Merck (Darmstadt,

---

* Corresponding author. Tel.: +98 311 3912351; fax: +98 311 3912350.
E-mail addresses: Ensafi@cc.iut.ac.ir, aaensafi@gmail.com (A.A. Ensafi).

http://dx.doi.org/10.1016/j.snb.2014.02.028
0925-4005/

Table 1
Comparison of analytical performance of our proposed H_2O_2 sensor with various non-enzymatic H_2O_2 sensors.

Working electrode	Linear range (μmol L^{-1})	Limit of detection (μmol L^{-1})	Working potential (V)	Reference
Pt-TeO_2-NWs	2.0–16,000	0.6	−0.20	[25]
PVA-MWCNTs-PtNPs	2.0–8000	0.7	0	[26]
Nafion/EGO/Co_3O_4-GCE	1–5000	0.3	0.76	[27]
Se/PtNPs	10–1500	3.1	−0.30	[28]
AgNP/SnO_2/GCE	10–35,000	5.0	−0.30	[19]
AgNPs/GCE	100–20,000	1.9	−0.30	[29]
RGO/Fe_3O_4/GCE	100–6000	3.2	−0.30	[30]
RGO/ZnO/GCE	0.02–22.5	0.02	−0.38	[31]
Pt-SnO_2@C	1–170	0.1	0.5	[32]
Cu/PSi-CPE	0.5–3780	0.27	−0.2	This work

Germany). All other chemicals were of analytical grade and used without further purification. Double distilled water was used for the preparation of all solutions. Britton–Robinson buffer was prepared by dissolving 5.0 g of boric acid, 2.7 mL of concentrated phosphoric acid (85%) and 2.3 mL glacial acetic acid in water and diluting to 1.0 L. Phosphate buffer solutions (0.1 mol L^{-1}) with different pH were prepared from H_3PO_4 and NaOH solution. Copper nanoparticles (CuNPs) were synthesized by wet chemical reduction procedure described elsewhere [33].

2.2. Apparatus

All electrochemical experiments were carried out by a computer controlled electrochemical analyzer (Autolab Model PGSTAT302N, Eco-Chemie, The Netherlands) with Nova-1.9 software. The standard three-electrode arrangement consisted of a saturated Ag/AgCl reference electrode, a platinum wire counter electrode and Cu/PSi-modified CPE as a working electrode was used. pH measurements were performed using a Corning pH-meter (Model 140) with a double junction glass electrode.

Fourier transform-IR spectrum was recorded using a JASCO FT-IR, 680 plus (Tokyo, Japan). PSi and Cu/PSi were characterized by X-ray diffraction with a Bruker D_8/advance X-ray diffraction (The Netherlands) with Cu-K radiation. The size of the copper nanoparticles and the morphology of Cu/PSi nanocomposite were observed by a field emission scanning electron microscope (FE-SEM, Hitachi S4160, Tokyo, Japan) at an accelerating voltage of 20 kV.

2.3. Synthesis of PSi & Cu/PSi nanocomposites

To prepare PSi powders, we used a commercially available Si-powder with a mean particle size of 40 μm. It was porosified *via* a chemical etching procedure described elsewhere [34]. Briefly, appropriate amount of Si-powder was dispersed in a solution containing HF, HNO_3 and H_2O with molar ratio of 4.0, 1.0 and 30, respectively. After mild stirring for about 10 min, the etching was finished and the initially gray color of Si powder turned to brown-yellow. The resulting powders were washed with distilled water until achieving a neutral pH and then dried at overnight to obtain PSi powder.

The electrodeless deposition of copper nanoparticles on 0.25 g of PSi was performed in a solution containing 0.05 mol L^{-1} copper sulfate and 0.1 mol L^{-1} HF (for about 20 min) to synthesis the Cu/PSi nanocomposite. The reduction of copper ions and the oxidation of surface Si involve electron transfer to the copper ions, those adsorbed at the surface of PSi from the surface atom. The corresponding half reactions can be expressed as:

$$Si + 6F^- \rightarrow SiF_6{}^{2-} + 4e^- \quad (1)$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (2)$$

Finally, the obtained nanocomposite (by filtration) was washed several times with distilled water and dried at room temperature overnight. The copper content of Cu/PSi nanocomposites was determined as 5.1%, using atomic absorption spectrometry.

2.4. Preparation of the sensors

Bare CPE was prepared by hand-mixing nujol oil and graphite powder with 70/30 (w/w) graphite/nujol oil. Cu-CPE was prepared by hand-mixing of 0.300 g nujol oil, 0.640 g graphite powder and 0.060 g CuNPs (the same percent for Cu/PSi-CPE). Cu/PSi-CPE was prepared by hand-mixing of 0.100 g Cu/PSi nanocomposite with 0.600 g of graphite powder in a mortar and pestle. Then, 0.30 g of nujol oil was added to the mixture and mixed well for 20 min until a uniformly wetted paste was obtained. The paste was packed into the end of an insulin syringe (i.d.: 2.0 mm) and an electrical contact was established *via* a stainless steel stick. Prior to use, a new surface was obtained by smoothing the electrode onto a weighing paper. PSi-CPE was fabricated using the same procedure as described above but a replacement of Cu/PSi nanocomposite with PSi.

3. Results and discussion

3.1. Characterization of Cu/PSi nanocomposite

The morphology of Cu/PSi nanocomposite was studied with FE-SEM. Fig. 1A clearly indicates that the copper nanoparticles are well deposited on the PSi surface and shows that Cu nanoparticles have an average particle diameter of about 67 nm. The crystalline structures of the products were identified with XRD (Fig. 1B). The diffraction peaks in PSi pattern ($2\theta = 47.2°$, 56.4°, 69.4° and 76.6°) can be assigned to Si(2 2 1), Si(3 1 1), Si(4 0 0) and Si(3 3 1), respectively. The diffraction peaks at $2\theta = 43.5°$, 50.7° and 74.8° in Cu/PSi pattern are indexed as the Cu(1 1 1), Cu(2 0 0), and Cu(2 2 0), respectively and indicating that Cu forms the typical face-centered cubic (fcc) crystal structure. The average particle size of Cu nanoparticles was calculated as 67 nm based on the peak width, using the Scherer equation. Other two peaks at 2θ of 36.7° and 61.6° suggested the existence of CuO in the Cu/PSi nanocomposite.

Fig. 1C shows FT-IR spectra of the PSi in the wavenumber range of 400–4000 cm^{-1}. The absorption peak of PSi located at 610–620 cm^{-1} is assigned to Si–Si stretching modes and the peaks in the range of 1000–1300 cm^{-1} are corresponding to the stretching modes of the Si–O–Si groups [35]. The weak peaks in the range of 2000–2300 cm^{-1} show that the outermost surface of the PSi consists of SiHx species [36]. The broad and intense band at 3450 cm^{-1} and the peak at 1630 cm^{-1} are possibly attributed to the stretching vibration and bending vibration of O–H groups, due to the structural hydroxyl group of SiOH and the presence of bound water or inhibited water [37]. It is found that Cu nanoparticles deposition on PSi causes no major change in the nature of the vibration modes or bonds present in PSi except in the reduction of overall intensity and