A new non-enzymatic glucose sensor based on copper/porous silicon nanocomposite

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ABSTRACT

Cu/PSi (copper/porous silicon) nanocomposite powder was prepared by chemical etching of silicon (Si) powder in a HF/HNO_3 solution, followed by electrodless plating of copper nanoparticles on the etched PSi powder in a solution containing $CuSO_4$ as a metal precursor. The resulting nanocomposite was characterized by X–ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV) and FT–IR spectroscopy. The copper nanoparticles in PSi support show the good chemical and electrochemical stability as well as electrocatalytic effect on Glc oxidation, hence the Cu/PSi nanocomposite was used to modify carbon paste electrode (CPE) to fabricate non-enzymatic Glc sensor. The electrocatalytic activity of Cu/PSi nanocomposite was investigated for Glc oxidation in alkaline and neutral solutions using cyclic voltammetry and chronoamperometry. The novel developed sensor displayed a fast amperometric response time of less than 4 s, long time stability, good signal reproducibility and two linear ranges from 1.0 to 190.0 $\mu mol\ dm^{-3}$ and 190 $\mu mol\ dm^{-3}$ to 2.3 $mmol\ dm^{-3}$ of Glc with a detection limit of 0.2 $\mu mol\ dm^{-3}$. The sensor exhibited no interference from common interferences such as ascorbic acid, dopamine, uric acid, fructose and citric acid. The good analytical performance, low cost and easy preparation method made this novel electrode material promising for the development of effective Glc sensor.

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1. Introduction

Porous silicon (PSi) is a promising material for various applications such as bio-technology [1], drug delivery [2], energetic materials [3] and catalysis [4]. PSi can be prepared by different methods such as anodic electrochemical etching [5], stain etching [6] and metal assisted electrodless chemical etching [7] in a HF-based solution. Very large specific surface area (that can attain 480 $m^2\ g^{-1}$) [8], the biocompatibility [9], and the possibility to modulate pore size and morphology by varying the formation parameters [10] has generated significant interest in PSi for chemical and biosensing applications [11–13]. Also PSi can be acts as a moderate reducing agent and a porous template for formation of noble metals/PSi nanocomposites and some researches on preparing metal/PSi nanocomposites have been reported [14,15]. Porous silicon was successfully used in the development of a quite large variety of new sensors, mainly using optical detection [16,17]. It is surprising that porous silicon electrochemical sensors didn't get as much attention as the optical sensors [18].

Reliable and fast monitoring of Glc has attracted much attention due to its significant index in clinical diagnoses, regulation of metabolism, and biochemical analysis [19–21]. Among various analytical methods, electrochemical sensors are attractive choice, due to its practicality, simplicity, and low-cost [22,23]. Currently, commercial Glc sensors rely on immobilized enzymes for selective recognition and quantitative analysis, but their inevitable drawbacks such as complicated and multistep immobilization procedures, chemical and thermal instabilities and pH-dependent response, have turned recent efforts to direct determination of Glc at non-enzymatic sensors [24]. Recently a review [25] about the usage of porous silicon in electrochemical sensors has been reported about the electrochemical detection of different drugs, DNA, bacteria and Glc. Based on our survey, surface functionalized silicon wafers have been used in all of these sensors. We used silicon microparticles (for the first time) to construct an electrochemical Glc sensor. For this purpose, copper nanoparticles were loaded on the etched silicon microparticles by a galvanic reaction. Because PSi can act as a reducing agent as well as porous template, this high surface porous material was used as a support for fast and facile synthesis of copper nanoparticles without adding any reducing agent. Also copper nanoparticles show good chemical and electrochemical stability on this support, which lead to good stability of the developed Cu/PSi nanocomposite based sensor. It is found that Cu/PSi nanocomposite has good electrocatalytic effect on Glc oxidation in 0.1 $mol\ dm^{-3}$ NaOH, leading to non-enzymatic Glc sensor with a detection limit of 0.2 $\mu mol\ dm^{-3}$.

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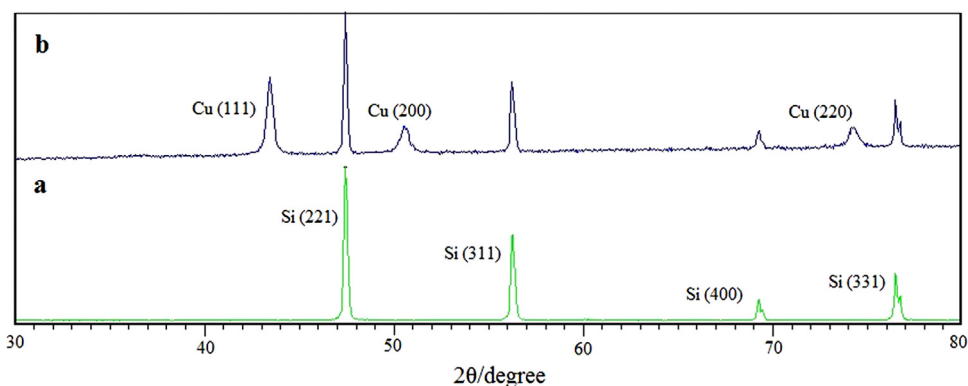*E-mail addresses:* Ensafi@cc.iut.ac.ir, aaensafi@gmail.com (A.A. Ensafi).

Fig. 1. XRD patterns of PSi (a) and Cu/PSi nanocomposite (b).

2. Experimental

2.1. Chemicals

Graphite, Nujol, sodium hydroxide, nitric acid, hydrofluoric acid, citric acid, Glc, sucrose, fructose and other chemicals were purchased from Merck. Polycrystalline Si powder (325 meshes, 99%) was purchased from Sigma-Aldrich. All other chemicals were of analytical grade and used without further purification. All the solutions were prepared with doubly distilled water. Phosphate solutions (0.1 mol dm^{-3}) were prepared by mixing of 25 mL of 0.25 mol dm^{-3} H_3PO_4 with different volumes of 0.5 mol dm^{-3} NaOH solution in a 100-mL volumetric flask and the flask was diluted to 100-mL with water.

2.2. Apparatus

An Autolab potentiostat-galvanostat, Model PGSTAT12 (Eco–Chemie, the Netherlands) controlled by a microcomputer with Nova–1.9 software was employed for all electrochemical experiments. A three-electrode electrochemical cell was used with a modified Cu/PSi–CPE as a working electrode, a platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode. A pH–meter (Corning, Model 140) with a double junction glass electrode was used to check the pH levels of the solutions.

The morphology of the samples was examined by a field emission Scanning electron microscope (FE-SEM, Hitachi S4160) at an accelerating voltage of 20 kV. X-ray diffraction (XRD) analysis was carried out with a Bruker D$_8$/Advance X–ray diffraction with Cu–K$_\alpha$ radiation. Fourier transform-IR Spectra were recorded using a JASCO FT-IR (680 plus). Specific surface area were measured from the nitrogen gas adsorption-desorption isotherms obtained using the Brunauer–Emmett–Teller (BET) method performed on Iran Nano Sord instrument.

2.3. Synthesis of PSi & Cu/PSi nanocomposites

PSi powders were prepared by chemical etching method [26]. Commercially available polycrystalline Si-powder was dispersed in an etching solution that consisted of HF, HNO$_3$ and H$_2$O with molar ratio 6, 1 and 30, respectively. After mild stirring for 20 min, the etching was finished and the initially metallic color of the powder was changed to brown-yellow. The obtained PSi was filtered and dried at room temperature for 24 h.

To synthesis Cu/PSi nanocomposite, copper nanoparticles were deposited on PSi surface by galvanic reactions from a 0.05 mol dm^{-3} copper sulfate solution containing 0.1 mol dm^{-3} HF with a controlled time of 5–30 min. The results showed that after 20 min, the copper nanocomposites well spread at the surface of the PSi. Longer

time causes aggregation of the copper nanocompostes at the PSi surfaces. The reduction of copper ions and the oxidation of surface Si involve electron transfer to the copper ions absorbed on the surface of PSi from the surface atom; the corresponding half reactions can be expressed as:

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

$$Cu^{2+} + 2e^- \rightarrow Cu \tag{2}$$

The resulting nanocomposite was filtered from the solution and dried in room air for 24 h. The mass content of the Cu in Cu/PSi nanocomposites were determined by atomic absorption spectroscopy (AAS) after dissolution of the nanocomposite. For this purpose, the copper content of the nanocomposite was dissolved in 3.0 mol dm^{-3} nitric acid and the amount of copper was determined by atomic absorption spectrometry. The result showed that about 5.3% w/w of the nanocomposite was copper.

2.4. Preparation of modified Cu/PSi–CPE and modified PSi–CPE

An unmodified CPE was fabricated by mixing of 0.30 g Nujol oil and 0.70 g graphite powder. Modified Cu/PSi–CPE was prepared by substituting corresponding amounts of the graphite powder (4, 8, 12, 16, 20% weight-to-weight ratio of the modifier relative to the graphite powder) by Cu/PSi nanocomposite and then adding the Nujol oil (0.30 g) and thoroughly hand-mixing in an agate mortar. Then, a portion of the uniform paste was packed firmly into the end of an insulin syringe (i.d.: 2 mm). The electrical contact was established with the copper stick. Prior to use, the surface of the prepared CPE was smoothed with a weighing paper.

The preparation process of the modified PSi–CPE was similar to that of the modified Cu/PSi–CPE but a replacement of Cu/PSi nanocomposite with PSi.

3. Results and discussion

3.1. Characterization of Cu/PSi nanocomposite

Five different methods including SEM, XRD, FT–IR, BET and CV were used to investigate the characteristics of PSi and Cu/PSi nanocomposite.

The XRD patterns of (a) PSi and (b) Cu/PSi nanocomposites are illustrated in Fig. 1. For PSi powder (Fig. 1a), four diffraction peaks are detected: 2θ = 47.4°, 56.3°, 69.2° and 76.5° [Si (221), Si (311), Si (400) and Si (331)], which are according to the literature [27]. The diffraction peaks at 2θ = 43.3°, 50.4° and 74.3° (Fig. 1 b) are indexed as the Cu (111), Cu (200), and Cu (220), respectively indicating that Cu forms the typical face-centered cubic (fcc) crystal structure [28].