



# Silver nanoparticles decorated anchored type ligands as new electrochemical sensors for glucose detection



M. Ghiaci, M. Tghizadeh, Ali A. Ensafi\*, Navid Zandi-Atashbar, B. Rezaei

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

## ARTICLE INFO

### Article history:

Received 27 September 2015

Revised 30 January 2016

Accepted 8 March 2016

Available online 25 March 2016

### Keywords:

Ag nanoparticles (AgNPs) decorated anchored type ligands  
Glucose oxidation  
Electrocatalysis  
Voltammetry

## ABSTRACT

This paper presents new two electrochemical sensors based on Ag nanoparticles (AgNPs) decorated anchored type ligands, those were prepared based on synthesizing of two amine compounds bounded to silica support, to detect glucose. These compounds were characterized using transmission electron microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy. TEM monitored AgNPs around 10 nm in size. These electrocatalytic properties of the modified carbon paste electrodes (CPES) were investigated by electrochemical techniques including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and hydrodynamic amperometry. According to amperometric studies, the better glucose sensor represented the detection range of 28.6  $\mu\text{mol/L}$  to 9.80 mmol/L glucose, with detection limit of 5.5  $\mu\text{mol/L}$  and sensitivity of 540.7  $\mu\text{A/mM}$ . In this work, three human blood serums were employed as real samples with satisfactory results.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Diabetes is known as a lasting illness causing metabolic and systemic disorders. A great number of people throughout the world suffer from diabetes so that this number is expected to raise two-fold in recent 20 years [1]. Diabetes is directly related to glucose levels of blood. Therefore, researchers have searched for fast, accurate, and stable approaches to analyze glucose levels, both *in vivo* and *in vitro*, not only in blood but also in other origins like nourishments and medications [2]. First report as enzymatic application of biosensors was developed in the decade of the 1960s [3]. Then, enzymatic electrochemical sensors on the basis of glucose oxidase (GOx) and horseradish peroxidase have been greatly explored to determine the glucose levels because of high sensitivity, specificity and low detection limit. These sensors suffer from poor reproducibility, thermal and chemical instability and high cost; however, they have been made by complex and multi-step immobilization to operate under critical conditions [4–7]. Moreover, these enzymatic sensors can be affected from environmental factors such as temperature, pH, and moistness and incompatible species like charged detergents [8]. Furthermore, electroanalysis by modified carbon paste electrodes represented further advantages including high sensitivity, low background current (compare to solid graphite or noble metal electrode), low

cost, more facile preparation and modification of the electrode by new materials, renewable surface, and possibilities of miniaturization [9]. Accordingly, non-enzymatic electrochemical sensors have been developed to directly measure the level of glucose in blood and other sources with stable and reliable responses [10–12].

Physical and chemical characterizations of metal nanoparticles (MNPs) compared to bulk ones have presented substantial differences, due to their large ratios of surface area to volume [13]. Since the application of MNPs suspensions represented some difficulties including aggregation, recovery and separation, the immobilization of MNPs on the supports such as silica, carbon nanotubes, clay, zeolites and  $\text{TiO}_2$  have been investigated [14–19]. In addition to high surface area, inertness and low cost of silica, it can be also anchored by bonding of organic groups to immobilize MNPs [19,20].

Herein, we present synthesis of two anchored type ligands to decorate silver nanoparticles (AgNPs). The AgNPs were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, and cyclic voltammetry (CV). The charge transfers of the electrodes were examined using electrochemical impedance spectroscopy (EIS) too. All investigations approved that the modified electrodes had better electrochemical properties relative to unmodified one. AgNPs decorated modified silica ( $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$  and  $\text{SiO}_2$ -pro- $\text{NH}_2$ ) were employed to analyze the glucose level as the non-enzymatic sensors. AgNPs decorated  $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$  carbon paste electrode represented low detection limit (LOD) of 5.5  $\mu\text{mol/L}$  glucose compared to the limit of detection of the other electrodes by value of 9.0  $\mu\text{mol/L}$  glucose.

\* Corresponding author. Tel.: +98 311 3913269; fax: +98 311 3912350.

E-mail address: [ensafi@cc.iut.ac.ir](mailto:ensafi@cc.iut.ac.ir), [ensafi@yahoo.com](mailto:ensafi@yahoo.com), [aaensafi@gmail.com](mailto:aaensafi@gmail.com) (A.A. Ensafi).

## 2. Experimental

### 2.1. Materials

Silver nitrate ( $\text{AgNO}_3$ ), glucose, silica gel ( $\text{SiO}_2$ ), graphite and paraffin oil were purchased from Merck. Ascorbic acid, uric acid, sucrose and fructose were provided from Sigma-Aldrich. All other reagents were of analytical grade and used without further purification. Phosphate buffer solutions (PBS, 0.1 mol/L) were prepared at various pHs by addition of NaOH to  $\text{H}_3\text{PO}_4$ . The water used throughout all experiments was twice distilled water. THF and toluene were initially distilled and dried using sodium metal in the presence of benzophenone as indicator.

Three human blood plasma were provided from Alzahra hospital (Isfahan, Iran) as real samples. The samples had been pretreated by filtering the contained proteins.

### 2.2. Apparatus

All electrochemical measurements were performed with an Autolab electrochemical analyzer, model PGSTAT-30 Potentiostat, Galvanostat (Eco-Chemie, Netherlands), controlled by a microcomputer. Data were acquired and processed using the GPES computer software 4.9.007. Electrochemical experiments were carried out at room temperature using a conventional three-electrode system with a modified CPE as the working electrode, a Pt rod as the auxiliary electrode and an Ag/AgCl/3.0 mol/L KCl as a reference electrode. Cyclic voltammetry (CV) experiments were carried out in quiescent solution at a scan rate of 100 mV/s in an electrochemical cell filled with 20.0 ml of 0.1 mol/L NaOH. The amperometric measurements were recorded at a hydrodynamic electrode with successive addition of glucose standard solution to the cell at an operating potential of 0.70 V. All electrochemical results were recorded when the surface of electrode became stable by 20 cycles of potential from  $-1.00$  to  $+1.00$  V.

The morphology of the nanoparticles was characterized by a transmission electron microscope (TEM) (TECNAI, Model F30, USA). The size distribution of the particles was determined by the analysis of TEM images using Digimizer software accompany with SPSS statistics (version 17.0). Fourier transform infrared spectra were recorded using FT-IR spectrometer (Jasco, FT/IR-680 Plus). All elemental compositions were analyzed by an elemental analyzer system (GmbH VarioEL V5.19.11, CHNS mode).

### 2.3. Procedure

#### 2.3.1. Synthesis of $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$

Silica-based anchored type ligand was synthesized as follow in Fig. 1: the silica gel was initially activated by heating during 3 h at a temperature of 500 °C, afterwards, the activated  $\text{SiO}_2$  was dispersed in dried toluene and refluxed with addition of 6.0 ml of 3-aminopropyltrimethoxysilane for 24 h. The obtained product was called  $\text{SiO}_2$ -pro- $\text{NH}_2$ . 0.80 g of the obtained solid and 1.10 g of cyanuric chloride were stirred for 24 h in a chilled medium of 3 ml of THF at temperature of 0 °C. This product was called  $\text{SiO}_2$ -pro-NH-cyanuric-Cl. The  $\text{SiO}_2$ -based anchored type ligand was produced by refluxing 0.20 g of  $\text{SiO}_2$ -pro-NH-cyanuric-Cl and 0.10 ml of 1,2-ethylenediamine in 5 ml  $\text{CCl}_4$  during 24 h at 60 °C, which named  $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$ . In each step, the solid was filtered and washed off with solvent and dried under vacuum at room temperature. The product of each step was therefore characterized by FT-IR spectrometer.

#### 2.3.2. Synthesis of AgNPs-decorated $\text{SiO}_2$ -pro- $\text{NH}_2$ (compound A)

0.10 g of  $\text{SiO}_2$ -pro- $\text{NH}_2$  was stirred in 2.0 ml of water until thoroughly dispersed. 1.0 ml of  $\text{AgNO}_3$  solution ( $1.0 \times 10^{-4}$  mol/L) was

slowly added to the former dispersion during 20 min. Silver ions were finally reduced to Ag nanoparticles (AgNPs) by addition of sufficient freshly prepared  $\text{NaBH}_4$  (0.10 mol/L). This product was rinsed several times with water and dried under vacuum at room temperature.

#### 2.3.3. Synthesis of AgNPs-decorated $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$ (compound B)

In the same way as compound A, 0.10 g of  $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$  was thoroughly dispersed in 2.0 ml of water. Then, 1.0 ml of the  $\text{AgNO}_3$  solution was added drop by drop to the mixture. After that,  $\text{Ag}^+$  ions were reduced to AgNPs by addition of the  $\text{NaBH}_4$  solution. The final product was washed and dried under vacuum at room temperature.

#### 2.3.4. Preparation of the modified carbon paste electrode (CPE)

To prepare two modified CPEs, 60 mg of graphite powder, 10 mg of compound A and/or compound B and 30 mg of paraffin oil were blended at a ratio of 6:1:3 (w/w) in the agate mortar for 20 min, to obtain a homogeneous mixture. The electrical connection was provided using the copper wire inserted through the paste. In the same way,  $\text{SiO}_2$  based carbon paste electrode was also prepared as a comparison index related to the electrodes of A/CPE and B/CPE. The CPEs was polished with a piece of weighing paper until the surface of the electrodes became uniform.

## 3. Result and discussion

### 3.1. Characterization of synthesized compounds

The methods including CHNS analysis, FT-IR, TEM, CV and EIS were employed to characterize compounds A and B. The CHNS analysis represents the weight ratio of the elements in compound A as 9.19% C, 1.79% H and 6.26% N, *i.e.* the molar ratio of C:H:N were 10:23:6, respectively while this molar ratio should be 10:21:8. This fact could therefore be caused from the yield of the reaction.

FT-IR spectra (Fig. 2) indicate the functional groups, which changed during the synthesis. The absorption band of  $1100\text{ cm}^{-1}$  placed in spectrum A is stretching vibration of Si–O–Si and the band of  $3200\text{--}3500\text{ cm}^{-1}$  implicated the stretching vibration of hydroxyl function of  $\text{SiO}_2$ ; The bands located at 2921–2940 and  $2840\text{--}2870\text{ cm}^{-1}$  are related to the stretching modes of  $-\text{CH}_2-$ , and N–H bond could be characterized by the band at  $1540\text{--}1560\text{ cm}^{-1}$  (as shown in the spectrum B); In spectrum C, the absorptions located in the range of  $1500\text{--}1700\text{ cm}^{-1}$  exhibit that an aromatic part is present in the structure, which could be related to the cyanuric ring. The N–H vibration is appeared around  $3000\text{ cm}^{-1}$  and the peak of  $1560\text{ cm}^{-1}$  is showed the stretching mode of N–H (as seen in spectrum D).

The formation of the AgNPs was investigated by transmission electron microscopy (TEM), as shown in Fig. 3A. The dark points are AgNPs, which are observed associated on the organic chain. In a general manner, the mean size of AgNPs, formed by this procedure, was estimated to be 10 nm with a nearly normal distribution (as exhibited in Fig. 3B), which was graphically analyzed by Digimizer software.

### 3.2. Electrochemical properties of the compounds A and B

Both cyclic voltammograms and electrochemical impedance spectra of the  $\text{SiO}_2$ /CPE, AgNPs-decorated  $\text{SiO}_2$ -pro- $\text{NH}_2$ /CPE (abbreviated by A/CPE) and AgNPs-decorated  $\text{SiO}_2$ -pro-NH-cyanuric- $\text{NH}_2$ /CPE (abbreviated by B/CPE) were studied as indicated in Fig. 4. Fig. 4A exhibits the recorded CVs of  $\text{SiO}_2$ /CPE (a), A/CPE (b) and B/CPE (c) those were obtained in alkaline medium of 0.1 mol/L

Download English Version:

<https://daneshyari.com/en/article/690386>

Download Persian Version:

<https://daneshyari.com/article/690386>

[Daneshyari.com](https://daneshyari.com)