Preparation and characterization of nickel oxide nanoparticles and their application in glucose and methanol sensing

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CHRONICLE	ABSTRACT
	In this work, a low cost glucose and methanol nonenzymatic sensor was prepared using nickel oxide (NiO) nanofilm electrodeposited on a bare Cu electrode. Electrochemical deposition was assisted with cetyl trimethylammonium bromide (CTAB) as a template. Scanning electron microscopy (SEM) was applied to observe the surface morphology of the modified electrode. Cyclic voltammetry (CV) and amperometry techniques were used to study the electrocatalytic behavior of NiO porous film in glucose and methanol detection. For glucose sensing, the electrode showed a linear relationship in the concentration range of 0.01-2.14 mM with a low limit of detection (LOD) 1.7 µM (signal/noise ratio (S/N)=3). Moreover, high sensitivities of 4.02 mA mM^{-1} cm^{-2} and 0.38 mA mM^{-1} cm^{-2} respectively in glucose and methanol monitoring suggested the modified electrode as an excellent sensor. The NiO-Cu modified electrode was relatively insensitive to common biological interferers. This sensor possessed good poison resistance towards chloride ions, and long term stability and significant selectivity towards glucose and methanol. Finally the proposed sensor was successfully applied for determination of glucose in human blood serum samples.

1. Introduction

Diabetes is a metabolic disorder, a major health problem all over the world and has affected more than 220 million people over the past few decades[1,2]. Electrochemical methods have potential application in the detection of D-(+)-glucose in blood samples[3]. Over the past decades, a number of studies have been conducted to reduce the disadvantages of enzymatic glucose sensors. The most common and serious problem was low stability due to the nature of the enzymes, which was hardly overcome. Although glucose oxidase (GOD) is quite stable compared with other enzymes, glucose sensors based on GOD are always vulnerable against thermal and chemical deformations during fabrication, storage or use. In addition, GOD quickly loses its activity in pH values below 2 and above 8 and temperatures above 40 °C can cause fatal damages[4]. To overcome the above obstacles, non-

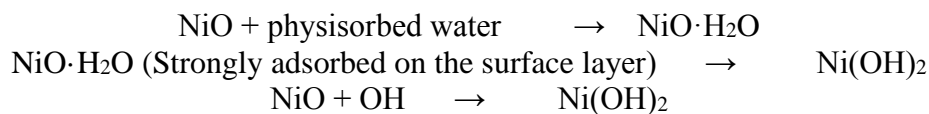enzymatic glucose sensors have been developed and kept coming closer to practical applications[5]. Methanol is one of the most commonly used volatile organic solvents, especially in industries and laboratories. Long-term exposure to methanol vapor could result in medical conditions such as headaches, eyesight disturbance and death. Therefore, the precise monitoring of the methanol concentration in a given environment is crucial. Developing a sensor that can rapidly and reliably evaluate methanol concentration is necessary[6]. Recently considerable researches have been concentrated on the use of low-cost metal oxide materials such as NiO[7-9], manganese oxide[10] and zinc oxide[11]. NiO has received a great attention because of its good electrochemical stability and electrocatalytic activity as well as low cost for a wide variety of applications[12]. In the present study, because of the large specific area and good electrocatalytic properties of NiO, the NiO-nanoparticles modified Cu electrode was investigated as an electrocatalyst for glucose and methanol determination in an alkaline media.

2. Results and Discussion

### 2.1. Fabrication and characterization of NiO modified electrode

The Ni film was directly deposited on an ultrasonically cleaned bare Cu electrode using CTAB as template. It is well known that CTAB can form different shapes at different concentrations in aqueous solution[13]. Under a negative applied potential of -1 V and in presence of CTAB as a soft template, Ni^{2+} ions, started to electrodeposit on the surface of the electrode in the form of Ni particles. The possible role of the CTAB is illustrated in Scheme 1. As shown in the scheme, Ni deposits had negative charge due to the adsorption of SO_4^{2-} ions. Therefore, the cationic surfactant (CTAB) interacted with negatively charged deposits through electrostatic cohesion. After washing the electrode surface with double distilled (DD) water, CTAB was removed from the surface and a porous nanostructured Ni film was appeared. In comparison with other physical/chemical methods for the fabrication of sensor electrodes, such as sputtering, electro-spinning, chemical vapor deposition, solvothermal synthesis and thermal decomposition, this electrodeposition route does not require complicated equipment and operations[14]. In the next step, the resulting electrode was immersed in 0.3 M NaOH solution to fabricate nickel oxides and also determine glucose and methanol. Use of porous films with non-uniform pores would result in better efficiency compared to traditional porous films[15]. Examination with SEM displayed a non-uniformed porous structure with nanoscaled morphology of the NiO deposits as shown in Fig. 1. The peak current of modified electrode and the redox peak potentials were almost equal after fifty scan. Therefore, we concluded that NiO film had good stability. The electrochemical reactions of Ni^{2+}/Ni^{3+} are as follows[16]:

$$NiO + \text{physisorbed water} \rightarrow NiO \cdot H_2O$$
$$NiO \cdot H_2O \text{ (Strongly adsorbed on the surface layer)} \rightarrow Ni(OH)_2$$
$$NiO + OH \rightarrow Ni(OH)_2$$

$Ni(OH)_2$ is extremely sensitive to electron exposure, and therefore, a pair of redox peaks appear due to the following reaction[16]:

$$Ni(OH)_2 + OH \leftrightarrow NiOOH + H_2O + e^-$$

For efficacy control, cyclic voltammograms of the bare Cu electrode and NiO modified Cu electrode were compared as shown in Fig. 2. According to Fig. 2 anodic and cathodic peaks were attributed to redox pairs Ni^{2+}/Ni^{3+} which was consistent with the results of the reference article[12]. The electrochemical behavior of the modified electrode was studied using CV technique.
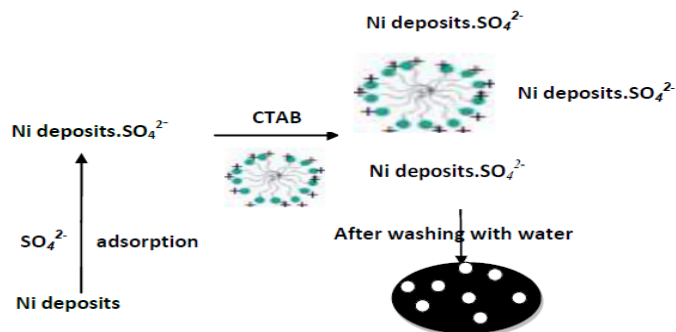
Scheme 1. Strategy for fabricating nanosized porous Ni film assisted with CTAB.
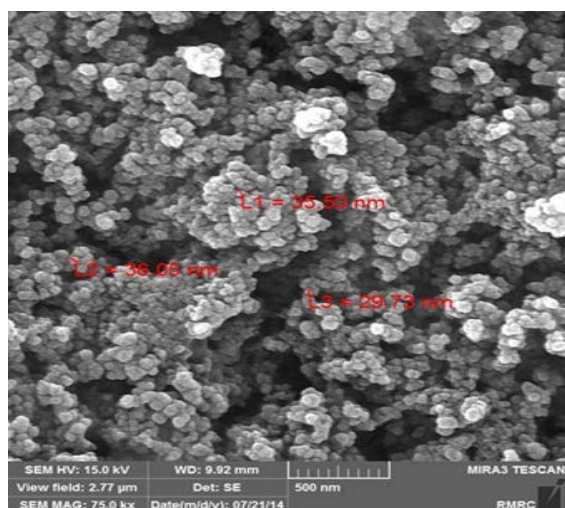

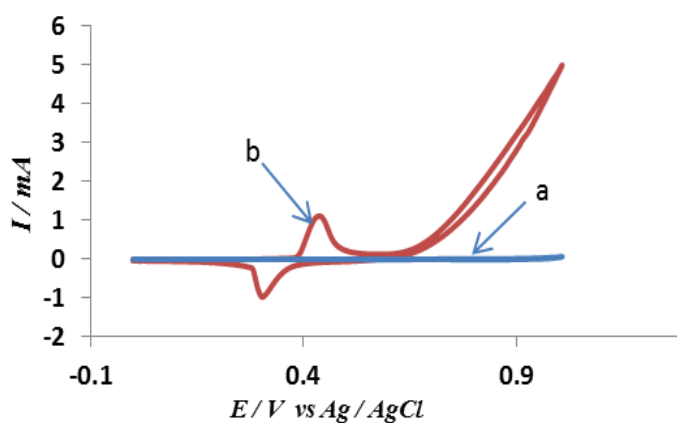**Fig. 1.** SEM image of the NiO modified electrode

Fig. 2. Comparison of cyclic voltammograms in 0.3 M NaOH solution: a) bare Cu electrode and b) NiO modified Cu electrode

2.2. Electro-oxidation behavior of glucose and methanol on the surface of nanostructured NiO modified electrode

In this work, NiO modified electrode was studied as an electrocatalyst in glucose and methanol sensing. Investigating electro-catalytic behavior of NiO towards glucose and methanol was accomplished with recording cyclic voltammograms at 0.05 $V \cdot s^{-1}$ in presence and absence of analysts. As shown in Fig. 3, in the presence of glucose an increase in anodic peak charge and reversely a light decrease in cathodic peak were observed which were indicative of an irreversible reaction on the electrode surface. Fig. 4 shows that increasing methanol concentration in the solution causes a linear increase in oxidation peak current. It should be mentioned that, in glucose and methanol determination, amperometry technique was applied rather than CV.

2.3. Amperometric detection of glucose with NiO modified electrode

All of the parameters which affected the experiments were optimized; i.e. $NiSO_4$, CTAB and NaOH concentration, applied potential and electrodeposition time of NiO film on electrode surface. Applied potential for amperometric detection of glucose and methanol was also optimized and $+0.5$ V was chosen as the best potential. Fig. 5 shows amperometric current response upon addition of different concentrations of glucose in 0.3 M NaOH electrolyte. According to Fig. 6 the electrode exhibited a linear relationship in the concentration range of 10 µM to 2.14 mM with a LOD of $0.0017 \pm (2/2 \times 10^{-4})$ mM (S/N=3, n=3 and confidence limit =95%) for glucose determination. The sensitivity of the sensor for glucose monitoring was calculated to be 4.02 $mA \cdot mM^{-1} cm^{-2}$ which is significant in comparison with values reported for graphene/NiO nanocomposites (1.57 $mA \cdot mM^{-1} \cdot cm^{-2}$)[12], Ni nanoparticles/SWNTs modified electrode (1.44 $mA \cdot mM^{-1} \cdot cm^{-2}$)[17], Cu_xO modified electrode (1.62

mA·mM^{-1}·cm^{-2})[18] and Cu$_2$O/SMWNTs modified electrode (2.14 mA mM^{-1}·cm^{-2})[19]. The performance of the prepared electrode in glucose detection was compared with those obtained from some other existing enzymeless glucose sensors. As shown in Table 1, the prepared sensor was the best among the compared sensors because of its excellent sensitivity, low LOD and wide linear range. Selectivity against interfering species is very important for a sensor. Amperometric current upon addition of glucose and common interfering species such as AA, UA and DA in biological samples is displayed in Fig. 6. For most of the nonenzymatic glucose sensors based on precious metals and alloys, the activity can be easily lost due to the poisoning of chloride ions[20,21]. Therefore, amperometric response of the modified electrode towards glucose was almost constant in 0.3 M NaOH electrolyte in the presence and absence of 0.45 M NaCl solution. Thus, the proposed sensor had significant poison-resistance ability towards high concentrations of chloride ions. Finally, the proposed nonenzymatic glucose sensor based on NiO-Cu electrode was applied to detect glucose in human blood serum samples at potential +0.5 V in 0.3 M NaOH using amperometric technique. Glucose concentration was found by drawing calibration curve. The response of the prepared electrode for glucose monitoring in real samples was confirmed well against the values obtained from a local hospital.
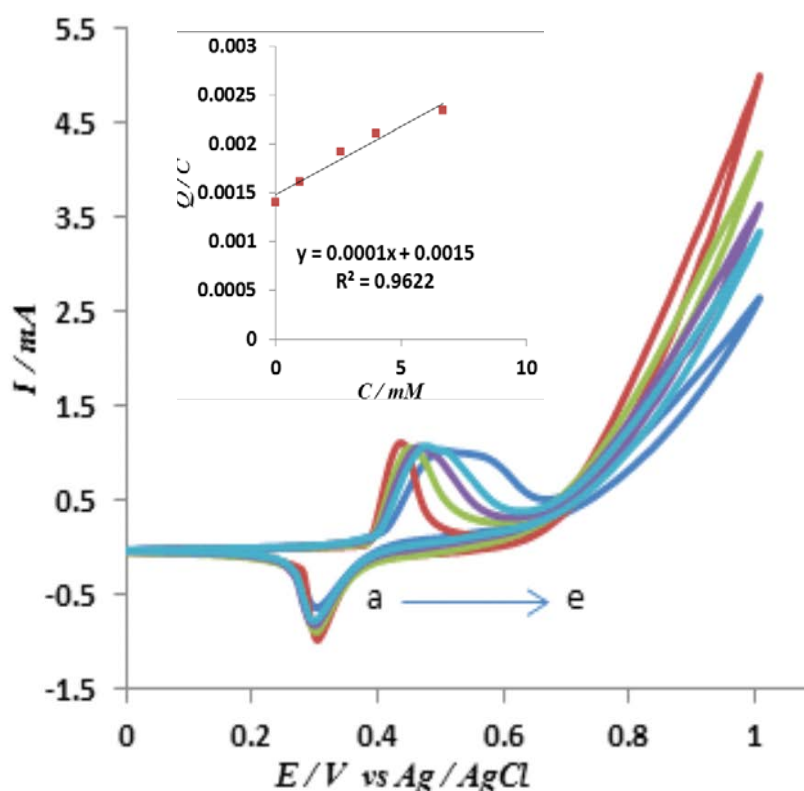

Fig. 3. Shows the cyclic voltammograms of modified electrode at 0.05 V·s^{-1} in 0.3 M NaOH electrolyte with glucose concentrations respectively: a) 0, b) 0.95, c) 2.61, d) 4 and e) 6.67 mM. The inset shows the plot of corresponding anodic peak charge versus glucose concentration
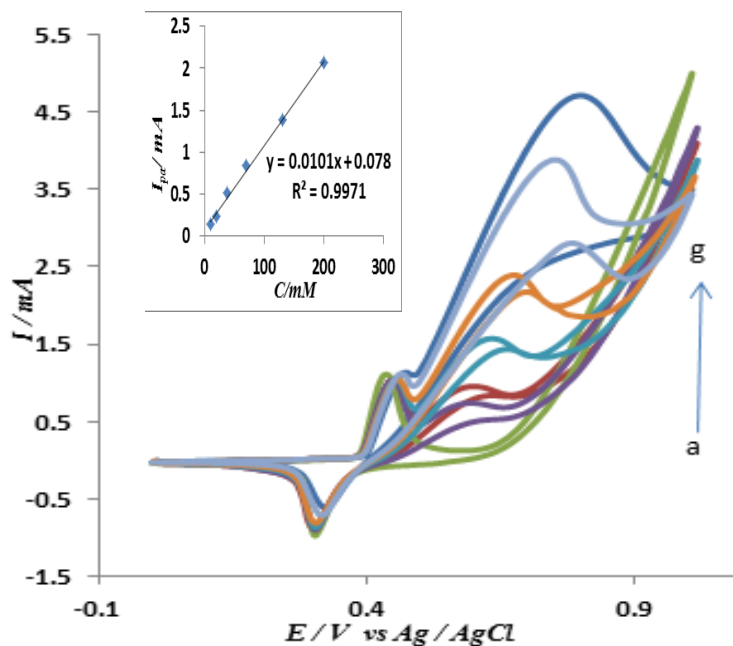
Fig. 4. Electro-oxidation behavior of modified electrode at 0.05 V s^{-1} in 0.3 M NaOH supporting electrolyte respectively: a) 0, b) 0.01, c) 0.02, d) 0.04, e) 0.07, f) 0.13 and g) 0.2 mM methanol. Inserted plots are relevant to cyclic voltammograms of Fig. 4
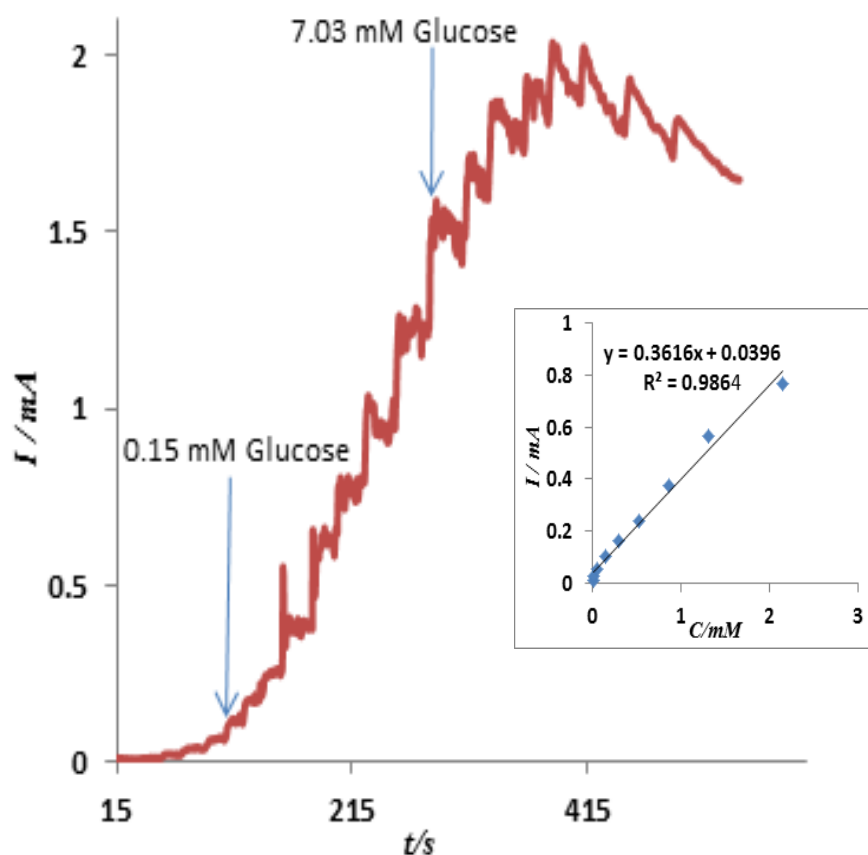

Fig. 5. Hydrodynamic amperogram upon addition of different concentrations of glucose in 0.3 M NaOH supporting electrolyte. The inset plot shows the corresponding calibration curve
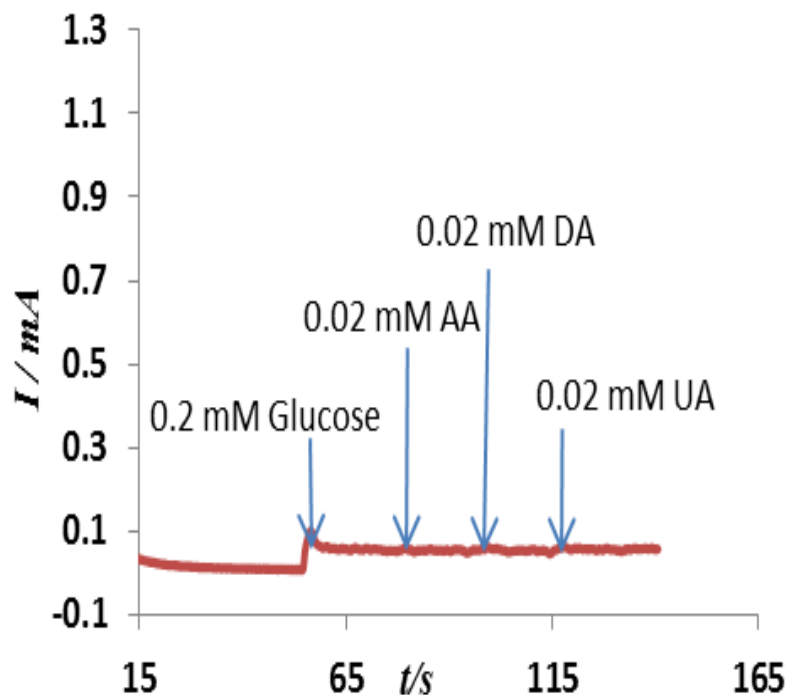
Fig. 6. Amperometric current upon addition of glucose and common interfering species

2.4. Amperometric detection of methanol with NiO modified electrode

The prepared sensor was also applied in methanol detection. Under optimized conditions applied potential of +0.5 V

Fig. 7a. Hydrodynamic amperogram of successive additions of methanol to 0.3 M NaOH electrolyte. b and c exhibit the amperometric current response versus methanol concentration (calibration curves)

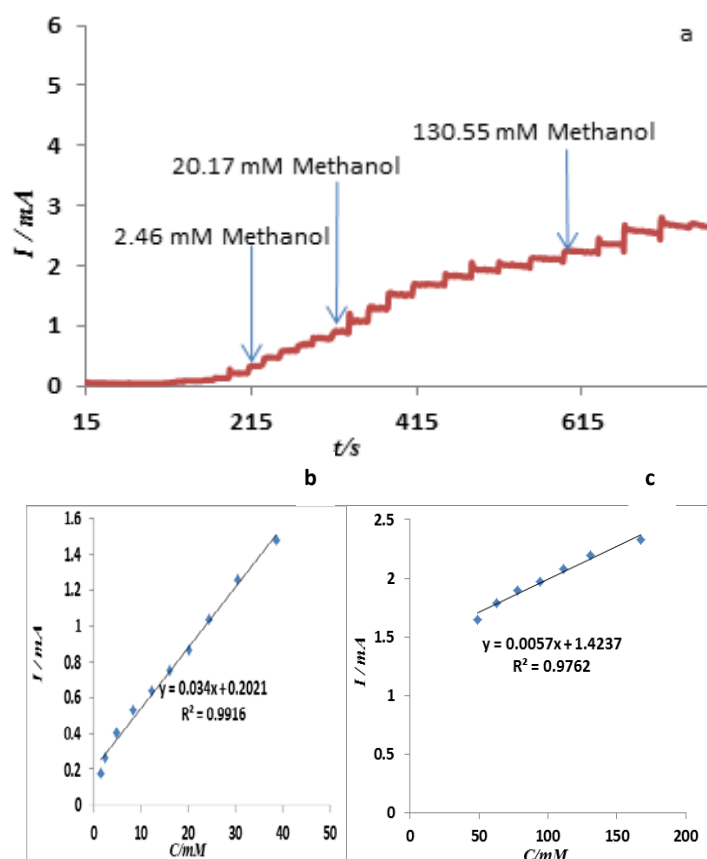Fig. 7a represents the successive addition of methanol to 0.3 M NaOH electrolyte. Figs. 7b and c exhibit corresponding calibration curves. This methanol sensor displayed two linear ranges from 1.50 to 38.57 mM and 49.28 to 167.06 mM with LOD of $0/82 \pm (1.1 \cdot 10^{-2})$ mM (S/N = 3, n = 3 and confidence level = 95%). The regression equation for the first linear range was I =0.034C+0.2021 with correlation coefficient of 0.9916. The sensitivity of the sensor for methanol detection was 0.38 mA mM^{-1} cm^{-2} which is very high in comparison with sensitivities of other methanol sensors such as: CEF-Ni(II)/Chitosan/GC (0.002 mA·mM^{-1}·cm^{-2})[22], Methanol dehydrogenase (0.02 mA·mM^{-1}·cm^{-2})[23] , etc. Comparison of the present NiO-Cu modified electrode with other existing methanol sensors is presented in Table 2; according to this table the proposed sensor is an excellent methanol sensor due to its high sensitivity and wide linear ranges. Thus, the facile fabrication and determination procedures based on electrochemically prepared NiO-Cu modified electrode provides enough potential for the sensor to be applicable in monitoring methanol concentration in the alcoholic beverages and other samples.

Table 1. Comparison of the present NiO-Cu modified electrode with other existing nonenzymatic glucose sensors

working electrode	Sensitivity (mA·mM^{-1}·cm^{-2})	LOD (µM)	Reference
NiO-Cu	4.02	1.7	This work
NiONPs/GO	1.09	1	[24]
CoOOH nanosheets	0.34	30.9	[25]
CS-RGO-NiNPs	3.18	4.4	[26]
GP/NiO	1.57	1	[12]

Table 2. Comparison of some parameters for methanol sensors

Working electrode	Sensitivity (mA·mM^{-1}·cm^{-2})	Linear range (mM)	Reference
NiO-Cu	0.38	1.50-38.57 and 49.28-167.06	This work
GP/NiO	0.002	0.2-24	[12]
Pt/CNTs	0.006	25–100	[27]
Twin Nafion membrane	0.06	500–2000	[28]

2.5. Stability and reproducibility of the sensor

Stability and reproducibility are two important factors for evaluating efficiency of sensors. In this research, stability of NiO modified electrode was evaluated over a one-month period. The sensor was stored at 4 ^{0}C in refrigerator and was tested each day for ten consecutive days and every five days over the next 20 days. The response of the developed sensor after one month was decreased only 5.6% and 6.3% respectively towards glucose and methanol detection according to amperometric current response. Moreover, we examined the reproducibility of the sensor by detecting amperometric current responses towards 0.08 mM glucose and 12.83 mM methanol in 0.3 M NaOH solution. The results of

7 repeated tests for each analyte indicated that the proposed sensor had acceptable reproducibility with a relative standard deviation (RSD) of 7.4% and 7.3% for glucose and methanol sensing respectively.

3. Conclusions

In this research, a new enzymeless sensor for methanol and glucose was fabricated based on NiO nanoparticles electrodeposited on a Cu electrode with CTAB as a soft template. The unique porous and nanostructured surface of the modified electrode enhanced the electro-catalytic behavior of NiO in methanol and glucose oxidation. As a result, the proposed sensor could be applied as a sensor owing to its high sensitivity in glucose (4.02 mA·mM^{-1}·cm^{-2}) and methanol (0.38 mA·mM^{-1}·cm^{-2}) detection, low LOD in glucose monitoring (1.7 µM) and two wide linear ranges (1.50-38.57 and 49.28-167.06 mM) in methanol sensing, low cost, facile preparation method, high stability, and satisfying precision and accuracy. On the other hand, the proposed sensor was successfully used in glucose monitoring in real samples.

4. Experimental

4.1. Materials and apparatus

D-(+)-Glucose monohydrate, methanol (99.99%), NiSO$_4$.6H$_2$O, NaOH, CTAB, AA, UA, DA and NaCl were all purchased from Merck. Blood serum sample was obtained from a local hospital. The 0.3 mol L^{-1} NaOH solution was used as supporting electrolyte for the electrochemical analysis. Double distilled (DD) water was used in all experiments. Electrochemical measurements were carried out on a µAutolab type III (made in the Netherlands). The surface of the electrode was cleaned with an ultrasonicator (parasonic mini, Pars Nahad Co., Iran). SEM images were obtained using a MIRA3 TESCAN SEM (Razi metallurgical research center (RMRC), Iran). All experiments were repeated at least three times.

4.2. Modified electrode fabrication

First, Cu electrode was polished by a 400 then 2000 grit emery paper, then the electrode surface was cleaned with ultrasonication in DD water for a few minutes and then the electrode was washed with DD water to remove surface impurities. In this study, porous Ni foam was generated on the bare Cu electrode using CTAB as a soft template in electrodeposition process. Under optimized conditions, the cleaned electrode was immersed into a mixture of 0.6 M NiSO$_4$ and 0.02 M CTAB, followed by an electrodeposition process with a constant potential of -1 V for 900 s, during which nickel nanoparticles were deposited on the surface of the electrode; afterwards, the Ni-Cu foam was rinsed with DD water and dried carefully in air for the next electrochemical experiment. In the second stage, the resulting electrode was immersed in 0.3 M NaOH solution and CV technique was performed at potential range 0.2–1 V until stable cyclic voltammograms were obtained. By doing so, Ni deposits were converted to NiO on the surface of the electrode. This modified electrode was used to evaluate glucose and methanol concentrations.

4.3. Electrochemical measurements

All of the tests were performed with a conventional three electrode system consisting of Cu electrode with 3 mm in diameter as a working electrode, and a Pt wire as a counter electrode; in this study all potentials were measured against Ag/AgCl electrode (KCl saturated). All of the experiments were performed in stationary state except amperometric measurements which were carried out by injecting analytes into 0.3 M NaOH solution while stirring constantly (150 rpm). All the experiments were accomplished at room temperature.

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