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# Silica template electrodeposition of copper oxide nanostructures on Ni foam as an ultrasensitive non-enzymatic glucose sensor

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## ABSTRACT

Silica templated copper oxide nanostructures were prepared on Ni foam electrode and presented as an enzyme-free glucose sensor. X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and field emission scanning electron microscopy (FE-SEM) techniques were used to characterize the presented electrode. A good synergistic effect between Cu and Ni for glucose determination caused a high sensitivity of 5.45 mA/mM/cm<sup>2</sup>, the linear range up to 22.5 mM and low practical detection limit of 4.81 nM. The electrochemical properties of the proposed sensor such as electrochemical active surface area, diffusion coefficient, and catalytic rate constant of glucose electro-oxidation were reported. The presented sensor showed good long term stability and reproducibility. It has excellent selectivity and it was applied for accurate determination of glucose in the real serum samples.

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## 1. Introduction

Sensitive and reliable glucose sensing is of paramount importance in clinical and food analysis. Enzymatic glucose biosensor has been accepted as an efficient and favorable choice due to its high selectivity. Glucose oxidase (GOx) and glucose dehydrogenase (GDH) frequently have been used for enzymatic detection of glucose, where glucose oxidase has played a leading role in enzymatic glucose biosensors due to more structural stability. Enzymatic glucose biosensors as hot topic, have been developed in three generations during three decades [1–3]. Although the presented enzymatic glucose sensors have high performances [4], but application of enzymatic based biosensors are limited by some shortcomings such as the relatively high cost, inherent instability, complicated immobilization procedures and critical operating and storage conditions. On the other hand, enzyme-free sensors which operate frequently in alkaline media, perform better than the enzyme-based sensors and exhibit improved sensitivity, stability, simplicity, reproducibility and detection limit. In addition, they are also less expensive. To evaluate enzyme-free glucose sensor need to focus on three challenges: (1) glucose diffusion at the electrode/electrolyte interface; (2) the catalytic behavior of the electrode materials; (3) the electron-transfer between the electrolyte and electrode [5].

Three dimensional electrodes by high surface nicely evaluate mass transfer. In non-enzymatic glucose sensor, some metals like Cu, Ni, Mn, Co and Fe are interested [6]. Ni foam (NF) as a three-dimensional porous platform has been used as an enzyme-free glucose sensor for the first time [7]. Ni as a non-noble metal has established by its effective electrocatalyst properties for glucose oxidation [8,9]. Modifying Ni foam by different metal oxides is [9–11] and mixed metal oxides [12,13] presented to increase surface area and evaluate electrocatalytic properties in electrochemical sensors area. Copper oxides nanostructure are interested in the non-enzymatic glucose sensors area due to their effective electrocatalytic activity [14–16]. Although modifying Ni foam with CuO nanostructures have been reported previously [16], but modifying technique has significant effect of sensor performance.

Nanostructures with significant surface area for modifying electrodes were interested in the electrochemical areas. Methods for nanostructure formation can be divided to template and template-free based methods. Mesoporous silica among templates is interested for producing nanostructures with tunable nanometer-scale diameters in a relatively simple fashion [17]. Recently developed electrochemically assisted self-assembly (EASA) method for mesoporous silica formation [18], combined synthesis and electrode modification steps. In EASA method, sol-gel films can be generated on the electrode surfaces by applying a suitable cathodic potential in the sol solution.

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In this work, the mesoporous silica film has formed by EASA procedure on the three-dimensional metal Ni foam electrode and copper oxide nanostructures were successfully prepared by using electrodeposition method in the silica templates. The proposed electrode was applied for the non-enzymatic glucose determination. The presented sensor displays fascinating sensitivity, low detection limit, and outstanding feasibility for real sample analysis.

## 2. Experimental

### 2.1. Materials and apparatus

Tetraethoxysilane (TEOS, 99%), HCl (36%, Merck), sodium nitrate (99%), ethanol (95–96%), cetyltrimethylammonium bromide (CTAB, 99%), copper sulfate pentahydrate (99%), sulfuric acid (98%), nickel nitrate hexahydrate (99%) and boric acid (99.5%) were purchased from Merck. Nickel foam from Liyuan Co. Electrochemical experiments were made by a three-electrode system was composed of modified Ni foam as a working electrode, Pt wire as counter electrode, and an Ag/AgCl (KCl 3M) reference electrode with  $\mu$ -Autolab potentiostat/galvanostat 101. The proposed electrode was studied with Electrochemical impedance spectroscopy (EIS) ZahnerEnnum, Field emission scanning electron microscopy (FESEM) TESCAN/Vega3, and X-ray diffraction (XRD)Equinox 3000, diffractometer equipped with Cu anode at 40 kV and 30 mA. The surface chemical states and compositions of samples were evaluated by X-ray photoelectron spectroscopy (XPS) analyses (XPS 1600E, PerkinElmer) using an Mg-K $\alpha$  excitation source. All the binding energy (BE) values were referenced to the C 1s line at 284.5 eV.

### 2.2. Electrode preparation

Ni foam was cut and sonicated in acetone for 10 min to remove any contaminants. Afterward, Ni foam was rinsed with water and bear 50 successive cyclic voltammetric scans in 0.1 M NaOH within  $-0.1$  to  $0.65$  V versus Ag/AgCl (KCl 3M) 50 mV/s to reach a reproducible cyclic voltammogram [7]. All current densities were normalized as a current / geometric area of the electrode. The electrode modification process has been presented in 2.2.1 to 2.2.3.

#### 2.2.1. Formation of mesoporous silica on Ni foam

Mesoporous silica film was electrodeposited on Ni foam with a starting sol solution consisting of 2 mL of 0.1 M NaNO<sub>3</sub>, 2 mL of ethanol, 1.36 mmol tetraethoxysilane (TEOS) and 0.43 mmol cetyltrimethylammonium bromide (CTAB). pH of the solution was kept 3 with suitable amount of HCl. The sol solution was allowed to hydrolyze for 2.5 h under stirring moderately prior to electrodeposition [18].

The mesoporous silica film was electrodeposited on Ni foam under potentiostatic conditions by applying a constant potential of  $-1.2$  V versus Ag/AgCl for 30 min in sol solution. Electrode rapidly was rinsed with water. The electrodeposited film on Ni foam was placed in an oven at 130 °C for 8 h. Afterward the electrode was placed in 0.1 M NH<sub>3</sub> over night to have more condensed silica spheres [19]. Finally, electrode was stirred moderately in 0.1 M hydrochloric acid in ethanol for 30 min to remove CTAB template.

#### 2.2.2. Electrochemical deposition of Cu and NiO into silica template

A solution of 0.1 M sulfuric acid solution containing 0.1 M copper sulfate and 0.04 M CTAB was prepared for CuO electrodeposition. Copper nanostructures electrodeposition was performed at a constant potential of  $-0.1$  V versus Ag/AgCl for 500 s. To form NiO nanostructure on Ni foam electrode the electrochemical cell solution contains 0.3 M nickel nitrate, 0.2 M boric acid, and 0.5 M sodium nitrate. The electrodeposition was performed at a potentiostatic mode in three electrode system at  $-1.0$  V versus Ag/AgCl for

10 min. at 50 °C. The prepared CuO/ NF and NiO/ NF arrays were annealed in air vented furnace at 400 °C for 2 h.

#### 2.2.3. Silica removing

Elimination of silica template was performed by 35 successive cyclic voltammetric scans in 3.0 M NaOH within  $-0.8$  to  $0.55$  V versus Ag/AgCl at scan rate 20 mV/s. Although silica dissolution in the concentrated NaOH in a long time, according to the bellow mechanism [20], but potential scans evaluate silica dissolution. In literature the effect of potential on silica/solution double layer was discussed [21].



## 3. Results and discussion

### 3.1. Silica film voltammetric study

To ensure formation of mesoporous silica film on Ni foam it is necessary to confirm with an electrochemical method. In this case, Fe(CN)<sub>6</sub><sup>3-</sup> as a negative and reversible electrochemical probe was chosen. As can be seen in Fig. S1 curve a, Fe(CN)<sub>6</sub><sup>3-</sup> has a reversible voltammogram on the Ni foam electrode. After the formation of mesoporous silica on Ni foam and before extraction of surfactant, Fe(CN)<sub>6</sub><sup>3-</sup> shows an insignificant response (Fig. S1 curve b). An insignificant response in Fig. S1 curve b indicates the pores are blocked and electron transfer of Fe(CN)<sub>6</sub><sup>3-</sup> is impossible. After removing surfactant template in Fig. S1 curve c, the electrode surface is accessible again via the pores. Indeed, the enhancement in the voltammetric current of the modified electrode with silica (Fig. S1, curve c) suggests a porous structure with good electrode accessibility [22]. The voltammetric currents of Fe(CN)<sub>6</sub><sup>3-</sup> on the modified electrode with the silica film were lower than the bare electrode (Fig. S1, curve a). In comparison, Fe(CN)<sub>6</sub><sup>3-</sup> shows higher peak to peak separation and lower anodic and cathodic currents after formation of silica on Ni foam electrode. This matter can be referred to electrostatic depletion of ferricyanide and negative charged silanol groups on the electrode surface [23,24].

### 3.2. Characterization of the prepared Ni foam electrode

The FESEM images were used to explore the surface structure of the prepared electrode in preparation steps. Fig. 1(a) and (b) shows that the NF has a 3-dimensional (3D) structure. Ni foam modified with mesoporous silica was displayed in Fig. 1(d) and (e) which demonstrates that porous structure was made on Ni foam. After the electrodeposition, the silica template was removed and the CuO nanostructures were observed. CuO nanostructures were formed on 3D Ni foam surface (Fig. 1g and h). As can be seen in Fig. 1(g) and (h) although the silica spheres were reduced due to treatment with NaOH, they were not removed completely.

Using CTAB additive in template-based method effect as capping agent and play a role in shaping small size CuO nanostructures at mild potential in the silica template [25]. The energy-dispersed spectroscopy (EDS) and XRD analysis were carried out on the prepared electrode and Figs. 1 and S2 clarify the formation of CuO nanostructures on Ni foam electrode. As can be seen in Fig. S2a, XRD pattern of Ni foam (top pattern) after modification with CuO nanostructures was varied to down pattern. In Fig. S2b, the XRD pattern of CuO/Ni foam has been shown with more details. The XRD patterns exhibit all of the major peaks at 44.5°, 51.8°, 76.4°, 92.8°, and 98.4° (marked with red circles) indicate cubic crystal system for Ni and the peaks at 38.1°, 44.4°, 64.6°, 76.1°, and 90.0° (marked with blue triangles) can be assigned to monoclinic structure for CuO. These results suggest that Ni foam was decorated with the CuO nanostructures.

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