



Electrocatalytic oxidation of glucose onto carbon paste electrode modified with nickel hydroxide decorated NaA nanozeolite



Seyed Karim Hassaninejad–Darzi ^{a,*}, Mostafa Rahimnejad ^b, Seyed Nima Mirzababaei ^a

^a Research Laboratory of Analytical & Organic Chemistry, Department of Chemistry, Faculty of Science, Babol University of Technology, Babol, P.O.Box: 47148-71167, Iran

^b Biofuel & Renewable Energy Research Center, Faculty of Chemical Engineering, Babol University of Technology, Babol, P.O.Box: 47148-71167, Iran

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ABSTRACT

In this study, a NaA nanozeolite was synthesized and characterized by an X-ray diffraction, scanning electron microscopy, nitrogen sorption and infrared spectroscopy. Crystal particle sizes of synthesized NaA nanozeolite were observed about 75 nm by SEM. Carbon paste electrode (CPE) was modified by NaA nanozeolite and Ni²⁺ ions. The electrocatalytic performance of the Ni-NaA/CPE toward glucose oxidation was evaluated by cyclic voltammetry, chronoamperometry, amperometry and differential pulsed voltammetry (DPV) techniques. The values of electron transfer coefficient, electrode surface coverage and charge-transfer rate constant for Ni(III)/Ni(II) redox couple were obtained to be 0.63, 3.98×10^{-8} mol cm⁻² and 0.126 s⁻¹, respectively. Also, the electron transfer coefficient, the diffusion coefficient and the mean value of catalytic rate constant for glucose and redox sites of electrode were found to be 0.86, 2.41×10^{-7} cm² s⁻¹ and 3.65×10^4 cm³ mol⁻¹ s⁻¹, respectively. The sensor was exhibited an acceptable linear range of 0.04–6.54 mM with detection limits of 1.98×10^{-3} mM (S/N = 3) by amperometric technique. Also, a linear range of 0.5 to 50.0 μM with detection limits of 0.02 μM was obtained by DPV method. The modified electrode (Ni-NaA/CPE) was successfully applied for the quantitative determination of glucose in blood serum samples by amperometric method and mean of recovery percentage was obtained to be 96.4%.

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1. Introduction

Oxidation of most carbohydrates, specially the reducing sugars, can be easily identified by electrochemical methods. However, their electrochemical oxidation is not easy and it requires a large overpotential on the conventional electrodes [1]. Glucose is a keen metabolite for living organisms, especially in the case of patients suffering from diabetes. Since Clark and Lyons reported the first enzyme electrode in 1962 [2], there has been considerable attention paid to developing new biosensors for the fast, reproducible, sensitive, and selective quantification of glucose. Electrochemical biosensors have been successfully applied for the determination of glucose. Glucose oxidase (GOx) is one of the celebrated enzyme for detection of glucose in solution due to its being stable, cheap and of practical use [3]. Most of the known glucose biosensors are fabricated based on the GOx, which can selectively catalyze the oxidation of glucose to gluconolactone which is hydrolyzed to gluconic acid and produce H₂O₂ in the presence of oxygen [4]. Quantification of glucose is achieved via electrochemical oxidation of the H₂O₂ since its concentration is directly proportional to the concentration of glucose in the sample. However, the oxidation of H₂O₂ usually requires a

relatively high positive potential usually over +0.824 V vs. NHE [5]. Application of GOx in biosensors also encouraged several problems. For example, activity of GOx can be easily affected by temperature, pH, toxic chemicals and humidity [5]. Also, a complicated procedure, including adsorption, cross-linking, entrapment, and electropolymerization, is required for the immobilization of the enzyme on the solid electrode and this may decrease the activity of the GOx [6].

Application of electrochemical methods using nonenzymatic materials for the glucose detection has several advantages compare with using enzyme, including stability, simplicity, reproducibility, inexpensive and free of oxygen limitation [6]. Considering these respects, the enzymless glucose sensor is an attractive alternative technique. Actually, many efforts have been tried for the determination of glucose without enzyme, including Pt electrode [7], Au nanoporous [8], NiO modified GCE [9], nickel electrode [10] and hierarchical Cu–Co–Ni electrode [11]. Also, modified carbon paste electrodes (CPEs) were used for determination of glucose without enzyme [12–14] and using enzyme [15]. Velarde et al. [16] studied oxidation of D-glucose with hydrogen peroxide as oxidant over several titanium-containing NaY zeolites. It is important to develop a nonenzymatic sensor that has high sensitivity and stability, and is interference free, for the determination of glucose by the method of electrochemical oxidation.

Fabrication of modified electrodes for electrocatalysis has been extensively developed and investigated by researchers. Modified

* Corresponding author.

E-mail address: hassaninejad@nit.ac.ir (S.K. Hassaninejad–Darzi).

electrodes provide an excellent way to accelerate charge transfer processes, decrease the overpotentials as well as to increase the intensity of the corresponding voltammetric responses [17]. Zeolites and nanozeolites are ordered porous crystalline materials with wide practical applications. They have high surface areas with strongly organized microporous channel systems that exhibit an advantage compared to other classical support materials [17]. One of the most representative artificial aluminosilicate zeolites, NaA zeolite (also called zeolite A or zeolite LTA), was firstly synthesized by the hydrothermal crystallization method and has been widely used in industry as catalysts, adsorbents, ion exchangers and zeolite membranes [18]. It is pointed out that zeolites and nanozeolites have been utilized in zeolite modified electrodes (ZMEs) and applied in electrocatalysis reaction [17].

Nickel is a relatively abundant and low price material that is utilized widely in numerous industrial applications. It is well established that Ni can be used as a catalyst based on its surface oxidation properties and has long-term stability in alkaline solutions [17]. Conversion of alcohols to carboxylic acids using a nickel electrode was firstly reported by Fleischmann et al. in 1971 [19]. Higher stability of the glucose sensors was achieved by the application of non-noble metals such as nickel. According to the literatures [20], the oxidation of glucose to gluconolactone (two hydrogen are liberated in this process) can be catalyzed by the NiOOH/Ni(OH)₂ redox couple at Ni electrode or modified electrode with nickel in the alkaline medium.

In respect of the literature survey, no NaA nanozeolite was employed for the modification of CPE for electrocatalytic oxidation of glucose. In this work, the NaA nanozeolite was synthesized and characterized by different techniques such as X-ray diffraction, scanning electron microscopy, nitrogen adsorption/desorption and infrared spectroscopy. Then, this novel nanozeolite was utilized for the modification of CPE and applied for electrocatalytic oxidation of glucose in the alkaline medium.

2. Materials and methods

2.1. Reagents and materials

Tetraethylorthosilicate (TEOS), sodium aluminate (NaAlO₂), sodium hydroxide, D-(+) glucose, potassium chloride, potassium hexacyanoferrate (K₄Fe(CN)₆) and nickel chloride hexahydrate (NiCl₂·6H₂O) were of analytical reagent grade and were purchased from Merck Company and used without further purification. Also, dopamine (DA), ascorbic acid (AA) and urea acid (UA) were used as received. Graphite powder and paraffin oil (density 0.88 g cm⁻³) as the binding agent (both from Daejung company) were used for preparing of the pastes. Also double distilled water was used throughout the experiment.

2.2. Preparation of organic template free NaA nanozeolite

NaA nanozeolite was synthesized by hydrothermal crystallization method using TEOS and NaAlO₂ as a silica and aluminum sources, respectively [21]. In a typical synthesis, 3.43 g of NaOH was dissolved in 51.4 mL of double distilled water. Then, 2.34 g of NaAlO₂ was added slowly to NaOH solution with stirring, followed by consecutive addition of double distilled water. Also, 5.9 mL of TEOS as an organic silica source was slowly added dropwise during 2 h and mixed with constant stirring. The molar composition of the above reactants was as follows: 1 Al₂O₃: 1.85 SiO₂: 3 Na₂O: 200 H₂O. After adding all the components, the above mixture was then transferred to Teflon-lined stainless steel autoclaves and heated at 453 K for 4 h under static condition. After this procedure, the product was separated by centrifuge (15,000 rpm), washed several times with double distilled water, dried overnight at 100 °C and calcinated at 550 °C for 5 h in the air.

2.3. Characterization

XRD pattern was recorded by an X-ray diffractometer instrument (XRD, GBC—MMA) with Be-filtered Cu K_α radiation (1.5418 Å) operating at 35.4 kV and 28 mA. The scanning range of 2θ was set between 5° and 70° with scan rate of 0.05°/s. The morphology and size of the synthesized zeolite were investigated with a scanning electron microscopy (SEM, VEGA2—TESCAN). Bruker FT-IR spectrometer (Vector 22) was used for gathering of Fourier transform infrared (FT-IR) spectrum at room temperature. Measurements of nitrogen adsorption/desorption at the temperature of liquid nitrogen were carried out using a volumetric adsorption equipment (Quantachrome Instruments, version 2.2). The specific surface area (S_{BET}) of the samples was evaluated with the Brunauer, Emmett and Teller (BET) method [22]. The electrochemical experiments were performed at room temperature using potentiostat/galvanostat electrochemical analyzer (Ivium, Netherlands, V11100) with a voltammetry cell in a three-electrode configuration. The Ag|AgCl|KCl (3 M) and platinum wire were used as reference and auxiliary electrodes, respectively. For better presentation, all potentials were reported with respect to the normal hydrogen electrode (NHE). The CPE and modified CPEs with NaA nanozeolites were used as working electrode in the electrochemical experiments.

2.4. Preparation of the working electrodes

For preparation of NaA/CPE, different amounts of NaA nanozeolite (5–30 wt% with respect to the graphite) were mixed with 200 mg of graphite powder and then paraffin oil (35 wt%) was blended with the mixture in a mortar by hand mixing for 30 min until a uniformly wetted paste was obtained. This paste was packed into the end of a glass tube (ca. 0.35 cm i.d. and 10 cm long) and the copper wire was used for electrical contact. A new surface was achieved by pushing an excess of the paste out of the tube and polishing with a weighing paper. For comparison, unmodified CPE without NaA nanozeolite (bare CPE) was also prepared in the same mentioned method.

2.5. Preparation of real samples

Human whole blood was obtained from local hospital and erythrocytes were separated from whole blood by removing the plasma. Human whole blood (2.0 mL) was first centrifuged for 10 min at 4000 rpm. The supernatant (plasma) was discarded and the rest was mixed with 5 mL of 0.9% NaCl solution. The solution was centrifuged for another 10 min at 4000 rpm and the supernatant (diluted plasma) was again discarded. The washing procedure with NaCl solution was repeated three times in order to remove the plasma almost completely. The erythrocyte pellets were hemolyzed with water (1:1, v/v). For protein precipitation, the hemolysate was mixed with 5-sulfosalicylic acid (10%, m/v) in the ratio of 2:1 (v/v). This mixture was centrifuged in the same condition described above. Then, determination of glucose in the supernatant was used by the fabricated electrode.

3. Results and discussion

3.1. Characterization of NaA nanozeolite

XRD powder pattern and SEM image of the synthesized NaA nanozeolite are presented in Fig. 1. The crystallization products matched the characteristic peaks of NaA nanozeolite at 2θ values of 7.2, 10.2, 12.4, 16.0, 17.4, 20.4, 21.7, 24.4, 27.2, 30.0, 34.2, 36.6 and 38.0 degrees that were reported by Treacy and Higgins [23], suggesting successful synthesis of NaA zeolite with good crystallinity. This result is in agreement with previous researcher's works in this area [24]. The XRD of NaA nanozeolite was indicated that space group of synthesized sample is Fm3c (no. 226) and a main diffraction peak at 2θ = 7.2° and

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