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A non-enzyme electrochemical qualitative and quantitative analyzing method for glucose, D-fructose, and sucrose utilizing Cu foam material

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ABSTRACT

In this paper, a non-enzyme electrochemical qualitative and quantitative analyzing method for glucose, D-fructose, and sucrose utilizing Cu foam material was explored. Three-dimensional (3-D) Cu foam material was prepared by electrochemical deposition method, and used as working electrode in the detecting system. Scanning electron microscopy (SEM) imaging results revealed the excellent characteristics of Cu foam, such as porous space structure and large specific surface area, which benefited detecting sensitivity by effectively enlarging contact area between electrode and chemicals. The experiments were performed in a conventional three-electrode setup using an electrochemical workstation. Cyclic voltammetry (CV) method explained the electro-oxidation process occurred on Cu foam electrode. Amperometric scanning results demonstrated that the detecting system fast responded (less than 10s) to glucose, D-fructose, and sucrose in the linear concentration range from 0.18 mM to 3.47 mM with the significant sensitivity of 3.39748 $mAcm^{-2}mM^{-1}$, 3.5811 $mAcm^{-2}mM^{-1}$, and 0.93192 $mAcm^{-2}mM^{-1}$, respectively. The limit of detection (LOD) is 12.96 μM, 12.3 μM, and 47.27 μM for glucose, D-fructose, and sucrose, respectively (S/N = 3). Cu foam electrode selectively responds to glucose, D-fructose, and sucrose against non-reducing chemicals (KCl and ethyl alcohol). Stochastic resonance (SR) signal-to-noise ratio (SNR) spectrum presented qualitatively discriminating ability for glucose, D-fructose, and sucrose.

1. Introduction

Sweetener plays an important role in human life. The ability to identify sweetener is particularly important as it provides animals with a means to find needed nutritive carbohydrates. Glucose, an important and widespread monosaccharide in nature, is the energy source of living cells and metabolic intermediate. With the development of social economics and improvement of human life standard, too much intake of glucose easily causes diabetes, obesity, etc. Glucose precise monitoring and control is importance for human life [1]. D-fructose, relating to caloric intake and fat accumulation, has equal importance with glucose to human health. However, fructose consumption is positively associated with increasing blood sugar, elevating triglycerides and systolic blood pressure [2]. Zavaroni et al. reported the mechanism of fructose-induced hypertriglyceridemia by fructose-fed rats experiment in 1982 [3]. Fructose intake by pregnant rats will cause a diminished maternal leptin response to fasting and refeeding and impairment in the transduction of the leptin signal in the fetuses, which can be responsible for their hepatic steatosis [4]. Sucrose, a kind of non-reducing disaccharide, is commonly used in foodstuffs and beverages. Jackson Jr. et al. reports that sucrose inhibits actin–myosin ATPase activity and actin sliding velocities [5].

Traditional instrumental sweetener analysis methods, such as high performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC-MS), are only suitable for laboratory analysis. The cost of these methods also limits their field usage. Moreover, skilled instrumental operators are specially required to conduct the operations. Electroanalytical techniques take unique advantages, such as high sensitivity, low LOD, low cost, and easy operations, etc, and develop fast in the past few decades. Electroanalytical glucose sensors can be classified into two types. One type is enzyme-based glucose sensor, and the other is non-enzyme based glucose sensor. In 1962, Clark et al. proposed the concept of enzyme-based glucose sensor, and reported the application of enzyme-modified electrode for glucose

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detection for the first time [6]. Due to the unique advantages in high sensitivity, good selectivity, low detection limit, and strong anti-interference, enzyme-based glucose sensors have been widely applied in clinical medicine, biochemistry, environmental monitoring, etc [7,8]. However, the main drawbacks of enzyme-based sensors include structural instability over long time, and narrow range of temperature. These drawbacks lead to the development of non-enzyme based glucose sensors. Pt, Cu, Ni, Au and their oxides are prepared as electrodes for glucose non-enzyme detection. Rong et al. constructed Pt/multi-walled carbon nanotubes (Pt-MWCNTs) electrode by dispersing Pt nanoparticles into MWCNTs for glucose detection in alkaline electrolyte [9]. Results revealed that modified Pt-MWCNTs electrode had good electrocatalytic characteristics towards glucose oxidation. The analysis results exhibited a linear concentration range of 1.0–26.5 mM under optimal analysis conditions. Bo et al. synthesized Pt modified multi-walled carbon nanotubes electrode by incorporating Pt nanoparticles into the mesopores of ordered mesoporous carbons (OMCs) for glucose detection [10]. Au and Pt-Au alloy perform high electrocatalytic activity and sensitivity, low detection limit in non-enzyme glucose analysis [11,12]. Up to now, several forms of Ni metal have been used in glucose sensors, such as Ni, Ni/Al, and Ni oxide (NiO), hydroxide ($Ni(OH)_2$), et al. Cu, Cu oxides, and Cu sulfides are also widely applied in electrochemical glucose analysis due to advantages including low cost, easy synthesis, and simple process. In recent years, great progress has been achieved in fructose sensor development. For example, a fructose sensor based on an osmium-polymer modified screen-printed graphene electrode (SPGE) was proposed for fructose detection [13]. A non-enzymatic electrochemical sensor based on a carbon paste electrode modified with electrospun $LaMnO_3$ fibers was also fabricated for fructose analysis [14]. In 2013, Vargas et al. assembled an amperometric sucrose sensor based on modified gold disk electrode to quantitatively determine sucrose, fructose and glucose in a continuous flow system [15]. These studies greatly promote sweetener detection techniques.

Much attention has been paid on 3-D Cu foam materials. In 2003, Shin et al. studied a new technique by electrochemical deposition accompanying hydrogen evolution to produce unique Cu foam [16]. However, self-made Cu foam was not ideally suited for fast electrochemical reactions because small pores near top surface might restrict the transportation of electroactive species (gas/ion) to inner space of the foam structure. In 2004, this group reported new foam structures by increasing pore size, which facilitated fast transport of electroactive gas (or ion) through porous electrodes. This method improved the sensitivity and selectivity of foam material. There is broad prospect of Cu foam material in chemical qualitative/quantitative analysis due to its unique electrochemical characteristics. Cu foam is mainly synthesized by electrochemical deposition, and the pore diameter is generally in micron range. While, most researchers focus on electrochemical deposition condition optimization. Recently, nonenzymatic glucose sensor based on Cu foam fabricated successfully [17]. The application of the Cu foam based sensor for glucose monitoring was successfully proposed.

A non-enzyme electrochemical glucose, D-fructose, and sucrose analyzing way utilizing Cu foam material was explored in this paper. 3-D Cu foam material was prepared by electrochemical deposition method, and used as working electrode. CV and amperometric i-t experiments were performed in a conventional three-electrode system utilizing electrochemical workstation at room temperature. KCl and ethyl alcohol were selected to evaluate detecting selectivity of Cu foam electrode to three sweeteners. CV scanning data of three sweeteners was processed by non-linear SR method. SR systematic output SNR spectrum qualitatively discriminated glucose, D-fructose, and sucrose successfully.

2. Materials and methods

2.1. Chemicals and reagents

NaOH and ethyl alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). D-glucose was purchased from Guangdong Guanghua Chemical Co. Ltd (Guangdong, China). D-fructose was commercially provided by Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). KCl was commercially provided by Chengdu Kelong Chemical Reagent Company (Sichuan, China). All the chemicals were of analytical reagent grade, and used without further purification. Deionized water was used during the experiments.

2.2. Cu foam preparation

Cu foam material was prepared using polyurethane substrates by electrodeposition. It was 1 mm in thickness and 70% in porosity. To increase the substrate surface functionalities and roughness, degreasing, roughening, sensitization, activation and peptization treatments were conducted. The treatments also benefit the remove of material surface contamination, and the reinforcement of physical/chemical properties. Then electroless copper plating was carried out in a mixture solution containing 12.0 g/L $CuSO_4 \cdot 5H_2O$, 42.0 g/L EDTA, 20.0 g/L Na_2SO_4, and 20.0 ml/L HCHO. Then electrodeposition was performed on the prepared polyurethane foam in the electroplate solution containing 70 g/L $CuSO_4 \cdot 5H_2O$, 0.6 g/L NaCl, 0.03 g/L polyethylene glycol, 0.05 g/L sodium lauryl sulfate, and 25 mL/L H_2SO_4. Foam material was utilized as cathode, and Cu plate was utilized as anode electrode in electrodeposition. DC power was used between cathode and anode to achieve unique Cu deposition. Finally, the achieved specimen was calcined at 600 °C temperature for excess polyurethane remove. Then it had hydrogen thermal reduction at 700 °C for 30 min. The obtained material was characterized by SEM scanning method.

2.3. Scanning electron microscopy (SEM)

SEM observation was performed using a SUPRA 55 SAPPHIRE instrument (Carl Zeiss Microscopy GmbH 73447 Oberkochen, Germany). InLens pattern and 5.00 kV was accepted.

2.4. Instrumentation

CHI-614E electrochemical workstation (CHI Instruments Company, China) was utilized to carry out amperometric i-t and CV measurement. Three-electrode system consisted of a platinum plate counter electrode, a Cu foam working electrode, and a 3 M KCl saturated Ag/AgCl reference electrode. The chemical solution was stirred by 85–2A stirrer (Xinrui Instrument, China).

2.5. Glucose, D-fructose, and sucrose quantitative measurement

CV and amperometric scanning was performed in glucose, D-fructose, and sucrose experiments. The geometric surface area of Cu foam immersed in NaOH supporting electrolyte was $0.25\ cm^2$. Taking 0.1 mM glucose as example, a potential range from −0.2 V to +0.7 V was utilized. CV scanning was performed at a scan rate of $50\ mV\ s^{-1}$. 15 ml 0.1 M NaOH mixed with 10 ml deionized water and 15 ml 0.1 M NaOH mixed with 0.1 mM glucose are used for CV scanning.

With 0.5 V applied potential, glucose amperometric i-t scanning was performed by continuously adding 0.045 mL 0.1 M glucose into 0.1 M NaOH every 50 s after mixing solution reached stable current