Applied Surface Science 465 (2019) 320–331

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Ultrasensitive and highly flexible nonenzymatic glucose biosensor based on laser-scribed carbon paper substrate

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ARTICLE INFO

Keywords:
Laser-scribed carbon paper
Cu network
Flexible biosensors
Glucose
Perspiration

ABSTRACT

Owing to the high specific surface area and easy accessability to targeting biomolecules, emerging non-noble-metal networks are developed as an ultra-active catalyst for molecular detection. In this work, a facile flexible enzyme-free glucose sensor with superior sensing performance has been successfully constructed by integrating laser-scribed carbon paper (LSCP) with copper network (CN). Remarkably, operation parameters are modeled and optimized by Central Composite Design (CCD) to obtain an optimal conductivity of 4.783×10^7 S·m^{-1} for CN. Due to the great electronic/ionic pathway between LSCP of ample active sites and CN of excellent conductivity, the disposable biosensor exhibits fast electron transfer kinetics. For glucose detection, LSCP/CN exhibits an excellent sensitivity of 3626.6 μA mM^{-1} cm^{-2}, a wide linear range from 1 μM to 7.96 mM, an ultra-low detection limit of 30 nM (S/N = 3) as well as favorable reusability. Satisfactory anti-interference capacity to electro-active oxides and selectivity against carbohydrates studied for concentrations up to normal physiologic levels and higher concentrations are systematically investigated. The applications of glucose determination in human serum and perspiration samples are also successful, with recoveries of 100.8% (± 2.28%) and 92.1% (± 3.61%), respectively. Experimentally, the current response of the LSCP/CN biosensor is resilient to mechanical deformation with less than 8% decay even after 1000 cycles of 1 mm repeated bending and 180° cyclical folding tests. As such, LSCP/CN can be applicable for flexible, attachable and potentially wearable biosensors to attain real-time physiological monitoring.

1. Introduction

The pursuit of fast, inexpensive, sensitive and reliable glucose (Gl) sensing has gained enormous attention due to its vital role in clinical application of Gl monitoring, environmental application of industrial waste water treatment and food application of dietary control. Emerging approaches including colorimetry [1], spectrophotometry [2] and chromatography [3,4] have been developed for Gl determination while the virtues of high sensitivity and time efficiency favor electrochemical sensor a more available candidate. For the enzymatic detection process, glucose oxidase can oxides Gl to gluconic acid in the existence of oxygen via direct electron transfer [5]. Nevertheless, the intrinsic instability of enzymes, high cost and demand of critical operational conditions compromise its serviceability for Gl detection [6–8]. Therefore, exploiting a simple, cost-effective and highly sensitive non-enzymatic Gl biosensor is significant and desirable.

Recently, various metal-based electrode materials, such as Au [9], Pt [10], Pd [11], Cu [12], Ni [13] and their metal oxides [14–16] have been investigated to construct high-performance non-enzymatic Gl biosensors. Among them, Cu-based nanomaterials exhibit remarkable electrocatalytic capability, good cost-effectiveness and reliable stability for Gl detection. There are mainly two methods to fabricate Cu nanoparticles including chemical synthesis [17] and electrochemical deposition [18]. The former method usually comprises of complex multistages such as hydrothermal treatment, addition of auxiliary polymer binders and high-temperature modification, which are energy-dissipating and further degrade the electron transfer efficiency of reactive materials. Comparatively, electroless deposition has been proven to be a useful, effective and convenient electrochemical approach for allowing the construction of metal networks onto various functional substrates [19].

The electrocatalytic capacity of CN varies greatly across electrodes with diverse surface characteristics and thus a functional substrate with large absorption area for depositing CN is indispensable for high-

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https://doi.org/10.1016/j.apsusc.2018.09.166
Received 25 June 2018; Received in revised form 11 September 2018; Accepted 20 September 2018
Available online 22 September 2018
0169-4332/

performance CN-based Gl biosensors. The Gl sensing catalysts are commonly supported by non-flexible substrates including glassy carbon [20], ITO [21] and Au [22], etc. Without sufficient flexibility, the applications of these substrates in multi-functional biosensors are largely hampered. Disposable, flexible and attachable electronics have attracted extensive attentions in the past decade while paper has been viewed as one key low-cost, environmentally friendly matrix for paper-based Gl biosensors [23–25]. Favorable tensile strength, good stiffness and low density prepare carbon paper (CP) a promising candidate to construct load-bearing composites. Individual carbon fibers of CP are well-connected and the conductive network and pore channels create an efficient electron percolation path as well as enable electrolytes access to the electrochemically active biomolecules without limiting charge transport [26,27].

In this work, copper networks (CN) are innovatively integrated with a flexible laser-scribed carbon paper (LSCP) substrate via a novel electroless plating process (EPP). Laser direct scribing (LDS) is performed to obtain laser-induced cavities and ruptures on the CP surface, which serve as highly active sites for further electrochemical reactions. Therefore, the LSCP/CN offers a large reactive surface area and absorption region, not only by increasing the electrolyte transfer rate, but also allowing a close contact between biomolecules and functional surfaces through wrinkled pores and channels. Central composite design in response surface methodology (CCD-RSM) is employed to investigate and optimize the effect of process parameters on the desired responses via statistical experimental optimization [28]. Parameters including laser fluence (E), scribing interval (S), pH of plating bath and plating time (t) are optimized by CCD-RSM for maximum conductivity of copper network. Thus in turn enhancing the corresponding current responses for glucose determination. Electrochemical measurements demonstrate LSCP/CN owns a high sensitivity, stability, and specificity for Gl oxidation with a wide dynamic range and a low detection limit. Remarkably, the sensing network possesses satisfactory anti-interference capability to common interfering species (ascorbic acid, uric acid, dopamine, acetaminophen and ethanol) together with favorable selectivity against other carbohydrates (maltose, xylose, lactose, fructose and sorbitol). LSCP/CN biosensor also shows good flexibility, the current response of the LSCP/CN biosensor is resilient to mechanical deformation with less than 8% decay even after 1000 cycles of 1 mm repeated bending and 180° cyclical folding tests. Successful application of the LSCP/CN for Gl determination in human serum and perspiration samples further render LSCP/CN a promising biosensor for in-situ, real-time and enzyme-free amperometric Gl sensing.

2. Experimental

2.1. Reagents and chemicals

Ethanol, D-(+)-Glucose, dopamine (DA), uric acid (UA), acetaminophen (AP) and ascorbic acid (AA) were provided by Beijing Chemical Works. Chloroauric acid ($HAuCl_4{\cdot}4H_2O$), sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from Aladdin Ltd. (Shanghai, China). Maltose, xylose, lactose, fructose, sorbitol and carbon paper were supplied by Taicang Biqi Novel Material Co., Ltd, China. All reagents were of analytical grade and used as received without further purification.

2.2. Construction of laser-scribed carbon paper (LSCP)

Carbon paper (CP) was modified by a simple and scalable laser direct scribing approach as depicted in our previous work with a few modifications [19]. Briefly, pristine CP was sequentially rinsed with ethanol, acetone and deionized water to remove any impurities which would hamper subsequent reactions. Then a 450 nm laser beam with a pulse width of 35 ns of home-made laser system was employed to engrave as-cleaned CP. A laser scribing software (Biqi 3.0) was used to adjust laser parameters and control the variables. The dimension of the scribing track regulated by a 2D galvanometer scanner was as-designed in 8.0 cm × 2.0 cm with 1 × 1 cm^2 sensing area.

Table 1
Independent variables and their levels used in the central composite design response surface model.

Independent variables	Factor level				
	−2	−1	0	1	2
Laser fluence ($J{\cdot}cm^{-2}$)	4	12	20	28	36
Scribing interval (μm)	1	6	11	16	21
pH of plating solution	7.0	8.5	10.0	11.5	13.0
Plating time (min)	7.5	20	32.5	45	57.5

2.3. Electrochemical integration of copper network

The copper network (CN) was decorated on the sensing area via a cost-effective electroless plating process (EPP). There were only two simple stages, namely, Au catalysts seeding and electroless copper depositing. Firstly, LSCP was soaked in Au colloid solution (prepared as shown in Table S1) for absorbing catalyst seedings. Au activated samples (abbreviated as Au-LSCP) were subsequently immersed in an electroless copper plating bath (prepared according to Table S2) to obtain metallization. After removing residual chemicals by deionized water and further dried at 50 °C in an oven, LSCP/CN was successfully fabricated in bright metallic color. Herein, four parameters including laser fluence (E), scribing interval (S), pH of plating bath (pH) and plating time (t) were optimized using CCD-RSM model as tabulated in Table 1. The whole fabrication process was illustrated in the Scheme 1.

2.4. Materials characterization

Image Pro Plus 6.0 software (Media Cybernetics, Carlsbad, CA) for Windows (a professional image analysis software) was employed to estimate the surface pore sizes and to pores distributions. Raman spectrometer (inVia, Renishaw, UK) was applied to characterize surface functional moieties of carbon paper samples in the whole process. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000C ESCA system (RBD upgraded) with Mg Ka radiation (h = 1253.6 eV). The high voltage was 14.0 kV and the current was 25 mA with a detection angle of 541. The pass energy was fixed at 23.5, 46.95 or 93.90 eV and the base pressure of the analyzer chamber was about 5 × 10^{-8} Pa to guarantee the required sensitivity and resolution. All the binding energies were calibrated to the C1s peak at 284.6 eV of the surface containment carbon. RBD AugerScan 3.21 software (RBD Enterprises, USA) was utilized to analyze the XPS data. With Cu Ka radiation (λ = 0.154 nm), the crystallinity of the metal nanocoating was determined by X-ray diffraction patterns (XRD) under a scanning speed of 0.1°/min. Field-emission scanning electron microscope (FESEM, FEG S4800) was used to observe surface morphologies, where attached energy dispersive X-ray spectroscopy (EDX) was utilized to perform elemental distribution analysis.

2.5. Electrochemical measurements

All electrochemical characterizations were performed on an electrochemical workstation (Chenhua Instrument, China) in a standard three-electrode system. Herein, LSCP/CN was used as the working electrode, with a platinum counter electrode and conventional Ag/AgCl reference electrode. Amperometric measurements were performed by consecutive addition of glucose into 0.1 M NaOH solution under constant stirring. The electrocatalytic performance of LSCP/CN was further evaluated with cyclic voltammetry (CV) and chronoamperometry.