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Electrochemical sensing interfaces with tunable porosity for nonenzymatic glucose detection: A Cu foam case

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ABSTRACT

It is widely thought in electro-biochemical analysis that the sensing interfaces play a key role in the enzymeless detection of biomolecules like glucose, ascorbic acid, dopamine and uric acid. On the way to maximize the anti-poisoning sensitivity of nonenzymatic electrochemical glucose sensors as well as achieve favorable selectivity, we propose here a porous interface fabricated by a facile but effective approach for glucose monitoring in alkaline media containing dissolved oxygen. The sensing interface based on porous Cu foams is directly formed on a homemade disposable screen-printed carbon electrode (SPCE) substrate by electrodeposition assisted with hydrogen evolution simultaneously, and its porosity can be easily tailored through adjusting deposition conditions for the optimal electrocatalytic oxidation of glucose molecules. SEM and BET studies show that the generated Cu foam possesses robust hierarchical porous architectures with greatly enhanced surface area and pore volume, beneficial for the unimpeded mobility of glucose and reaction products. Cyclic voltammetric tests indicate that a diffusion-controlled glucose electro-oxidation reaction occurs at the Cu foam electrode at around +0.35 V vs. Ag/AgCl in 0.1 M NaOH. Chronoamperometric results obtained under optimized conditions reveal that the proposed sensor exhibits desired poison resistance ability in the presence of chloride ions and significant selectivity to glucose, providing fascinating sensitivities of 2.57 and 1.81 mA cm^{-2} mM^{-1} for glucose in the linear concentration ranges of 2–80 μM and 0.1–5 mM, respectively. The limit of detection is calculated to be as low as 0.98 μM according to the signal-to-noise ratio of three. In addition, the fabricated sensing interface shows attractive reproducibility (RSD of 5.1% and 7.0% for 15 repeated measurements on a sensor and for measurements on 15 prepared sensors, respectively) and outstanding long-term stability (less than 5% loss in sensitivity over 1 month) for glucose detection. The application of the Cu foam based sensor for monitoring glucose in practical samples is also successfully demonstrated.

1. Introduction

In past decades sensing of glucose has always been the hotspot in the biochemical analysis field because of its scientific and technological importance in clinical diagnosis and individual blood sugar management as well as food and pharmaceutical monitoring, environmental pollution inspection and bioprocess control (Heller and Feldman, 2008; Wang, 2008). In this context, development of glucose detection devices with high sensitivity, good selectivity, rapid response, low cost and easy-to-use properties draws a plenty of academic and commercial attention and interest (Kimmel et al., 2012; Niu et al., 2013). Since the first enzyme-modified electrode was reported by Clark and Lyons (1962) for glucose determination with selectivity, enzyme glucose biosensors, especially glucose oxidase (GO*x*) based sensors, have been well commercialized for wide use in diabetes control, thanks to a variety of technological improvements on the immobilization of enzymes and the design of electron-mediator systems (Hu, 2009; Newman and Turner, 2005). Due to the highly selective catalysis behavior of enzymes and the gained technological advances, GO*x*-based biosensors are able to provide excellent selectivity along with sufficient sensitivity for glucose sensing in clinical applications. In spite of these positives, the common commercialized enzyme-based glucose detection devices still expose a few insurmountable drawbacks: the essential prerequisite of a biocompatible matrix as the

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support, the fussy procedures for immobilization or entrapment of enzymes on the matrix, and the high cost of enzymes fade the glamour of enzyme-based sensors; (Bankar et al., 2009; Park et al., 2006) more seriously, the vulnerable stability of GO*x*-based sensors hardly makes them survive under harsh thermal, chemical and pH milieu due to the nature of enzymes, simultaneously resulting in the mediocre precision and reproducibility of measurements and the rigor for test strip storage (Park et al., 2006; Toghill and Compton, 2010; Wilson and Turner, 1992). In this case, it is also not advisable to apply enzyme-based sensors to monitor glucose in sophisticated and uncertain circumstances (Niu et al., 2013). Based on these considerations, increasing interest has been focused on the realization of efficiently electrochemical glucose sensing without using any enzyme for the last couple of decades (Park et al., 2006). It is generally believed that the electrochemical sensing interface constructed by electrode materials and structures plays a crucial role in enzymeless analysis, and hence assembling beneficial electrochemical interfaces to facilitate the electrocatalytic glucose oxidation reaction with faster diffusion and kinetics at lower overpotential is of foremost focus (Toghill and Compton, 2010).

Owing to their outstanding redox properties at different potential ranges under various reaction conditions, transition metals (Cu, Ni, Fe, Co, Mn, etc.) as well as their oxides and sulfides attract a mass of attention as electrode materials for nonenzymatic glucose sensing in alkaline solutions (Cao and Wang, 2011; Chen et al., 2008; Li et al., 2010; Liu and Xue, 2011; Lu et al., 2009; Niu et al., 2013; Wang et al., 2012a, 2012c; Xia and Ning, 2010; Zhou et al., 2013). Among these materials, Cu and its chalcogenides are of particular interest for electro-oxidizing glucose due to their minimal cost and ease of synthesis and post-handling (Meher and Rao, 2013). More importantly, they are able to catalyze the electrochemically glucose oxidation reaction with large kinetics rates thanks to the flexible switch of valence states on Cu-based sensing interfaces. Therefore, Cu metal with a variety of dimensionalities and micro/nanostructures including nanocubes, (Zhao et al., 2013) flowers, (Zhao et al., 2012) octahedral cages (Zhao et al., 2012) and dendrites, (Chen et al., 2012) various Cu_xO (Li et al., 2010; Meher and Rao, 2013; Wang et al., 2012b; Zhang et al., 2010; Zhuang et al., 2008) and Cu_xS (Liu and Xue, 2011; Qian et al., 2013; Zhang et al., 2008, 2012) as well as other Cu-based compounds (Sim et al., 2012; Zhou et al., 2013) have been frequently used to fabricate enzyme-free electrochemical glucose sensors with good sensitivity, selectivity and poisoning tolerance. Many efforts are also made to introduce combinations of transition metals and oxides (Ding et al., 2012; Noh et al., 2012; Tong et al., 2010; Zhang et al., 2011) along with fascinating supports like conducting polymers, (Meng et al., 2013) carbon nanotubes (Dung et al., 2013; Yang et al., 2012) and graphene (Luo et al., 2012) to enhance the performance for glucose detection. Nevertheless, an assortment of examples suggest that these unsupported and supported micro/nanostructured Cu materials are weak in mechanical stability and durability of performance, because they easily suffer from agglomeration, deformation, segregation and collapse of structures for extended periods of time under applied potential, thus diminishing the efficiency for glucose sensing (Niu et al., 2013). Besides, lack of suitable pores of the Cu-based structures makes it hard for glucose molecules and reaction products to get access to and escape from the electroactive sites, which reduces the sensitivity, selectivity and anti-poisoning activity of the fabricated sensors during long-term duration operation (Meher and Rao, 2013). Moreover, maximizing the sensitivity of nonenzymatic electrochemical glucose sensors as well as achieving favorable selectivity is always welcome.

With the above concerns, we recommend here a captivating electrochemical sensing interface assembled by porous Cu foams for enzymeless glucose determination. The Cu foam based interface is *in situ* formed on a homemade disposable screen-printed carbon electrode (SPCE) substrate by electrodeposition assisted with hydrogen evolution. The advantages of this interface for nonenzymatic analysis of glucose are multi-fold: (1) the used electrodeposition is a facile but effective way to reproducibly prepare the Cu foams; (2) the synthesized Cu materials are directly generated on the disposable substrates, and no post-synthesis treatment and further immobilization of materials are required; (3) the formed Cu foam possesses hierarchical porous architectures with largely enhanced surface area and pore volume, which is very beneficial for the unimpeded mobility of glucose and reaction products; (4) the Cu foam is supposed to be mechanical stable during long duration measurements due to the robust crisscrossed scaffolds that originate from the 'hand-in-hand' foam walls; and (5) the porosity of the sensing interface can be expediently tailored for the optimal glucose sensing through adjusting the electrodeposition conditions. With these positives, the systematic electrochemical studies indicate that the fabricated electrochemical interface based on porous Cu foams shows attractive sensitivity, excellent selectivity for glucose and against other species, good long-term stability and great possibility for practical applications during enzymeless glucose detection.

2. Experimental

2.1. Chemicals

$CuSO_4$, H_2SO_4, NaOH and NaCl were purchased from Sinopharm Chemical Reagent Co. and used directly without further purification. D-glucose, D-xylose, D-galactose, D-fructose, D-mannose, L-arabinose, D-ribose, L-rhamnose, L-ascorbic acid, dopamine, uric acid and 4-acetamidophenol were commercially provided by Sigma-Aldrich. All analyte stock solutions were stored in 4 °C overnight for sufficient mutarotation before utilization. Ultrapure water (18.2 MΩ cm, Laboratory Water Purification Systems) was used during all experiments. All other chemicals were of analytical grade and utilized as received.

2.2. Fabrication of the Cu foam based sensing interfaces

In the present research, the porous Cu foams were *in situ* generated on the homemade disposable SPCE substrates using the hydrogen evolution assisted electrodeposition approach. The detailed printing procedures of SPCEs had been described in our previous reports, (Niu et al., 2012; Teng et al., 2009) and their configuration with the working region being 3 mm in diameter was illustrated in Fig. S1 (Supporting information). All electrodeposition experiments were carried out on a CHI440A electrochemical workstation (CH Instruments, Inc.) equipped with a conventional three-electrode setup consisting of a SPCE working electrode, a Pt wire counter electrode and a 3 M KCl saturated Ag/AgCl reference electrode. Before electrodeposition, the newly prepared SPCE substrates were electrochemically anodized by cyclic voltammetric scanning from +1.5 to +2.0 V for 40 segments. In a typical synthesis, the anodized SPCE was immersed into a mixture of 0.2 M $CuSO_4$ and 0.5 M H_2SO_4 for 15 min, to allow the precursor solution to contact with the substrate surface adequately; then an electrodeposition process with a constant potential of -6 V was performed for 30 s, and during this course hydrogen bubbles were liberated along with Cu deposition; afterwards, the resulting electrode was carefully rinsed with ultrapure water and dried in air for characterization and electrochemical measurements.