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Electrochemical fabrication of stalactite-like copper micropillar arrays via surface rebuilding for ultrasensitive nonenzymatic sensing of glucose

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ABSTRACT

In this work, an ultrasensitive nonenzymatic amperometric glucose sensor was facilely constructed based on a novel stalactite-like copper micropillar array, which was fabricated by surface rebuilding of a smooth Cu electrode in a blank H_2SO_4 electrolyte without using templates and precursor solutions. During repeated square wave potential pulse perturbation, the smooth surface of Cu electrode was reshaped into a thin film of aggregated nanoparticles, assembled microspheres and then stalactite-like Cu micropillar arrays consisting of layered irregular Cu nanoflakes through repeated electrodissolution/electrodeposition of Cu. This is similar to the natural formation processes of stalactites that involve repeated dissolution/precipitation of $CaCO_3$. Moreover, the accompanying evolution of hydrogen bubbles led to the pillar arrays porous. Such micro/nanostructured Cu pillar arrays are beneficial both for surface reactions and for mass transport. The influence of pulse potential, pulse frequency, perturbation time, and electrolyte concentration on the electrocatalytic activity of the treated Cu electrode was investigated in detail. The Cu pillar arrays not only had better electrocatalytic activity for oxidation of glucose than the aggregated Cu nanoparticles and assembled Cu microspheres, but also showed excellent electrochemical performance in sensing glucose with a wide linear range (500 nM~4.711 mM), short response time (5 s), ultrasensitivity (2432 $\mu A\,mM^{-1}\,cm^{-2}$), low detection limit (190 nM), good anti-interference and anti-toxicity, long-term stability (over 4 weeks), and satisfactory quantification of glucose concentration in human serum.

1. Introduction

Owing to its scientific and technological importance in clinical diagnosis [1], individual blood glucose management [2], food and drug monitoring [3], environmental pollution inspection [4], and bioprocess control [5], glucose sensing has become a hotspot in the field of biochemical analysis [6]. Compared with other analytical methods such as spectroscopy [7], chromatography [8], colorimetry [9,10], and photoelectrochemisty [11], electrochemical biosensors have more extensive application prospect due to their many advantages such as high sensitivity, good selectivity, rapid response, low cost, and easy to carry and use [6].

Since the first glucose biosensor based on enzyme electrode reported by Clark and Lyons [12], much progress has been made on electrochemical glucose sensors with enzymes due to development of immobilization procedures of enzymes, electron carrier systems [13], and nanomaterials [6]. Although enzymatic glucose sensors have high selectivity and enough sensitivity, they also expose some disadvantages such as complicated immobilization procedures, high cost, easy inactivation, and sensitive to temperature, pH, humidity and toxic chemicals [13,14]. To address these shortcomings, nonenzymatic glucose detection has aroused more and more interests as an alternative [14].

So far, many micro/nanomaterials have been fabricated to construct nonenzymatic glucose sensors such as carbons, noble metals (Au, Ag, Pd and Pt), cheaper metals (Cu, Ni, Fe, Co, and Mn) as well as their oxides and sulfides [15–22], and Cu-, Ni- or CoO-coated nanoporous Au [23–25]. Among them, Cu micro/nanomaterials that involve Cu(II)/Cu(III) redox pair are an attractive platform for nonenzymatic glucose sensing due to their low cost, fast kinetics, and facile preparation. CuO nanowires [26], CuO nanospheres [27], CuO nanoflowers [28], CuS nanotubes [21], Cu

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foams [29], and Cu-coated nanoporous Au [23] are representative examples that were used in nonenzymatic glucose sensing. Notably, porous structures are beneficial due to their enlarged surface area for reactions and charge transport, plentiful channels for mass transport, and the structural effects such as discriminative electrokinetics, nano-confinement, electrical double layer overlapping, ion-selective impedance, etc [30–32].

In this work, we fabricated a novel micro/nanostructured stalactite-like Cu pillar array on a Cu electrode for nonenzymatic glucose sensing simply by rebuilding the smooth surface of Cu electrode with square wave potential pulse perturbation in a blank H_2SO_4 solution. The main merits of this new micro/nanostructured stalactite-like Cu pillar array for nonenzymatic glucose sensing include these points: (1) its fabrication involves repeated electrodissolution/electrodepoation of Cu, similar to the natural formation processes of stalactites from repeated dissolution/precipitation of $CaCO_3$; (2) it is derived directly from the smooth Cu surface, and no precursor solutions, templates, and post-treatment/immobilization are required; (3) it is structurally stable from the reshaping; (4) the pillar array has large surface area, abundant active sites from the layered irregular nanoflakes, and plentiful porous channels between pillars, which benefit surface reactions and mass transport. Therefore, the new micro/nanostructured stalactite-like Cu pillar arrays significantly enhanced electrocatalytic activity for oxidation of glucose in comparison with the aggregated Cu nanoparticles and assembled microspheres that formed during the surface reshaping. The as-proposed sensor based on Cu pillar arrays demonstrates excellent performances in nonenzymatic sensing of glucose and provides precise quantification of glucose concentration in human serum.

2. Experimental

2.1. Reagents and instruments

D-(+)-glucose (Glu) ($C_6H_{12}O_6 \cdot H_2O$), L-ascorbic acid (AA) ($C_6H_8O_6$, 99%) and uric acid (UA) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), Guangdong Xilong Chemical Co. Ltd (Guangzhou, China) and Sigma, respectively. Other reagents were analytical pure and used without further purification. All solutions were prepared with Millipore ultrapure water.

Electrochemical experiments were performed on a CHI 660 C electrochemical station (Chenhua Instruments, Shanghai, China) with a three-electrode system including a copper disk (2 mm diameter, purity $\geq$99.8%) as working electrode, a circle platinum wire or a Pt plate as counter electrode and a saturated mercurous sulfate electrode (SMSE) as reference electrode.

Surface morphological images of the prepared electrode were taken by a Quanta FEG 250 scanning electron microscope (SEM) operated at 10 kV. The crystalline phases were analyzed by a Bruker D8 Discover micro-area X-ray diffractometer (XRD) using Cu *Kα* radiation ($\lambda = 0.1542$ nm). Surface composition of the electrode was analyzed by X-ray photoelectron spectroscopy (XPS) on a K-Alpha 1063 spectroscope operating at 12 kV with Al *Kα* monochromatic radiation.

2.2. Fabrication of copper pillar arrays

Before fabrication, the copper electrode was successively polished with metallographic sandpaper (1200 mesh) and α-alumina powders (50 nm) to a mirror-like surface, then sonicated three times each for 3 min in Millipore water. Optimally, square wave potential pulses with a frequency of 10 Hz between 0 V and −1.4 V were applied on the smooth Cu electrode immersed in a 1 M H_2SO_4 solution for 5000 s to produce copper pillar arrays. During preparation, the surface of working electrode was placed upwards to facilitate the release of hydrogen bubbles. The as-prepared copper pillar array electrode was rinsed three times each for 30 min in Millipore water before use or characterization. The detailed results for optimization of pulse potential, pulse frequency, perturbation time, and H_2SO_4 concentration in treating Cu electrode are provided in Supplementary Data from Fig. S1 to Fig. S5, which were based on the electrocatalytic activity for oxidation of glucose.

2.3. Electrocatalytic oxidation and sensing of glucose

The copper pillar array electrode was evaluated as a glucose sensor in 0.1 M NaOH solution. Cyclic voltammograms (CVs) were measured to compare the electrocatalytic oxidation behavior for glucose on the treated Cu electrodes by varying the treated time, pulse potential range, pulse frequency and electrolyte concentration. Amperometric curves were obtained at designed potentials while the solution was kept stirring. All electrochemical experiments were operated at room temperature.

3. Results and discussion

3.1. Fabrication mechanism of copper pillar arrays

Fig. 1 shows the cyclic voltammogram of smooth Cu electrode in 1 M H_2SO_4, which is consistent with previous results [33]. During the positive potential scan, oxidation current started to ascend at −0.4 V for dissolution of copper electrode with a current peak around 0.1 V. Two-step single electron transfer reactions (Reactions (1) and (2) took place successively with potential increase, generating Cu(I) and Cu(II) species [33–37]:

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \quad (1)$$

$$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^- \quad (2)$$

The Cu_2O on the electrode surface did not diffuse into solution and could undergo chemical oxidation in a lesser extent by dissolved oxygen molecules according to Reaction (3):

$$Cu_2O + (1/2)O_2 \rightarrow 2CuO \quad (3)$$

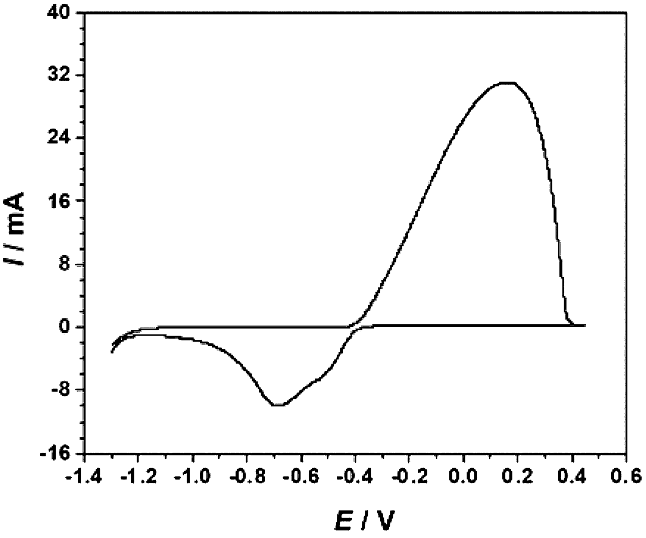

Fig. 1. The cyclic voltammogram at 100 mV s^{-1} on smooth Cu electrode in 1 M H_2SO_4 solution.