



High-performance hybrid electrode decorated by well-aligned nanograss arrays for glucose sensing



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ABSTRACT

The worldwide boost in glucose related diseases such as diabetics over the last decade leads to an overwhelming demand for development of advanced electrochemical glucose sensors with high sensitivity, fast response and excellent selectivity. Herein we report a novel freestanding microelectrode comprising well-aligned $\text{Cu}(\text{OH})_2$ nanograss arrays and uniform nanoporous copper (NPC) substrate. Such a cost-effective hierarchical hybrid structure entails a unique combination of good conductivity of NPC and high electrocatalytic activity of $\text{Cu}(\text{OH})_2$. As a result, the glucose sensor based on the hybrid nanostructure exhibits extraordinary performance towards the oxidation of glucose with a high sensitivity of $\sim 2.09 \text{ mA cm}^{-2} \text{ mM}^{-1}$, wide linear range of 0.2–9 mM, low detection limit of 197 nM, fast response time of less than 1 s and excellent selectivity. The current work not only provides novel hybrid materials with great potential to be commercialized in blood glucose sensing, but also has important implications for designing enhanced nanostructured electrocatalysts for engineering applications in general.

1. Introduction

Electrochemical sensors have recently attracted extensive attention because of their great potential applications in the fields of bioprocess monitoring, diabetes management and medical diagnosis (Chaudhuri and Lovley, 2003; Heller and Feldman, 2008; Newman and Turner, 2005; Ronkainen et al., 2010; Wang, 2001, 2008; Yoo and Lee, 2010). Especially, the increase of diabetics over the last decade requests urgent development and improvement of high-performance electrochemical glucose sensors (Control and Prevention, 2014). The sensing performance of the electrochemical glucose sensors indispensably requires not only an efficient transport of glucoses and electrons, but also a fast redox reaction at the electrode/electrolyte interface (Minteer et al., 2012; Park et al., 2006; Yang et al., 2010). In other words, desirable electrodes of the electrochemical glucose sensors should concurrently possess good electric conductivity and high catalytic activity so that good electrocatalytic performance for probing glucose can be achieved. Recently, nanostructured transition metal oxides or hydroxides have demonstrated their potential as effective electrode candidates for electrochemical glucose sensors owing to their low cost, high catalytic activity and good biocompatibility (Dong et al., 2012; Si et al., 2011; Solanki et al., 2011; Subramanian et al., 2014; Sun et al., 2015; Ye et al., 2012; Zhang et al., 2014). For example, $\text{Cu}(\text{OH})_2$ nanocatalyst exhibit extraordinary electrochemical activity of fast response and high

sensitivity due to the redox pair of $\text{Cu}(\text{OH})_2/\text{CuOOH}$ in which CuOOH can be deoxidized by glucose directly (Singh et al., 2009; Zhou et al., 2013). Nevertheless, the non-uniform/uncontrollable micro-morphology and poor electric conductivity limit their wide application in glucose sensing. Currently, noble nanoporous metals and micro/nanoparticles have been explored as conductive pathways for increasing the electrocatalytic performance of the transition metal oxides and hydroxides catalysts (Chen et al., 2010; Ding et al., 2011; Lang et al., 2013; Wang et al., 2008; Yehezkeili et al., 2011; Zhai et al., 2013). However, the high cost of these precious metals and complex electrode construction hinder their widespread uses.

In this paper, we report synthesis of the unique hybrid nanostructure composed of well-aligned $\text{Cu}(\text{OH})_2$ nanograss arrays grown on economic nanoporous copper (NPC) substrate. The $\text{Cu}(\text{OH})_2$ nanograss array (NGA) and the NPC substrate enable high electrocatalytic activity and good conductivity, respectively. Compared with conventional $\text{Cu}(\text{OH})_2$ nanowires or nanofibers, the hierarchical NGA@NPC hybrid can be flexibly prepared in the form of bulk and free-standing thin films with open nanoporosity, high specific surface area and high electric conductivity, and thus can be directly used as electrodes in detecting glucose. As expected, the hierarchical hybrid electrode exhibits prominent comprehensive performance in detecting glucose, which is characterized by a unique combination of ultrahigh sensitivity, wide linear dynamic range, ultra-low detection limit, fast response time and

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long-term stability. Moreover, such hybrid structures are cost effective due to easy electrode construction and cheap raw materials. All of these advantageousness makes the current hybrid structure extremely promising for commercial applications in electrochemical blood glucose sensors.

2. Experimental

2.1. Reagents and chemicals

Sodium hydroxide (NaOH), hydrofluoric acid (HF), ammonium persulfate ($(\text{N}_2\text{H}_4)_2\text{S}_2\text{O}_8$), glucose, lactose, sucrose, maltose, and fructose were purchased from Sinopharm Chemical Reagent Co., Ltd. Uric acid (UA) and ascorbic acid (AA) were supplied by Sigma. Nafion® perfluorinated resin solution (5 wt% in mixture of lower aliphatic alcohols and H_2O) was provided by Sigma-Aldrich. All chemicals were of analytical grade and used without further purification. Human serum samples were obtained from the university hospital at University of Science and Technology Beijing. Deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was generated by a Barnstead water system.

2.2. Synthesis of NPC thin films

The method of producing NPC thin film was described in our previous report (Li et al., 2016). Briefly, glassy precursor of the $\text{Cu}_{60}\text{Zr}_{35}\text{Al}_5$ (nominal atomic percentage) ribbons were prepared by a melt-spinning technique under a high purity argon atmosphere. The NPC thin films were produced by chemical dealloying the $\text{Cu}_{60}\text{Zr}_{35}\text{Al}_5$ glassy precursor in a dilute HF aqueous solution (10 mM) at room temperature for 24 h. The dealloyed products were rinsed with deionized water and dehydrated alcohol repeatedly to remove residual chemical substances within pore channels.

2.3. Fabrication of $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid

The $\text{Cu}(\text{OH})_2$ NGA@NPC hybrids were synthesized by an alkaline oxidative method in which the cleaned NPC thin films were placed in an aqueous mixture of 0.1 M $(\text{N}_2\text{H}_4)_2\text{S}_2\text{O}_8$ and 0.3 M NaOH for different reaction times to grow $\text{Cu}(\text{OH})_2$ NGA. When the surface of the NPC films turned light blue, they were taken out of the solution, thoroughly rinsed with ultrapure water and dehydrated alcohol repeatedly and finally dried in air.

2.4. Microstructure characterization

X-ray diffraction (XRD, Rigaku DMAX-RB-12 kW, $\text{Cu-K}\alpha$) was used to determine crystal structures of the nanostructured samples. Scanning electron microscopy (SEM, Zeiss Auriga, Germany) and transmission electron microscope (TEM, Tecnai G2 F30) were used to characterize microstructure and chemical composition of the as-fabricated NPC thin films and $\text{Cu}(\text{OH})_2$ NGA@NPC hybrids. For the TEM studies, as-prepared NPC and hybrid specimens were dispersed by sonication in dehydrated alcohol and the resultant suspensions were put onto holey carbon-supported copper grids. X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA-DLD, Kratos) with an Al $\text{K}\alpha$ (mono, 1486.6 eV) anode at an energy level of 150 W in a vacuum of 10^{-7} Pa was employed to investigate surface chemical state and binding energy of the samples. The specific surface area and pore size distribution of the products were measured using a BET analyzer (Quadrasorb SI) at 77 K.

2.5. Evaluation of electrocatalytic performance

All electrochemical measurements including cyclic voltammetry and amperometric titration tests were performed using an electrochemical workstation (ACM instrument, GillAC) with a conventional three-electrode system at room temperature. The system was

constructed using the $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid as working electrodes, a platinum plate as the counter electrode and a Ag/AgCl standard electrode (3 M KCl) as the reference electrode. 0.1 M NaOH aqueous supporting electrolyte and other analyte solutions with different concentrations were freshly prepared. To remove oxygen, the solutions were purged with high-purity N_2 for 1 h before testing. The amperometric response tests of glucose were carried out at an applied potential, and the analyte solutions were injected into the electrolyte after the current curve reached a steady baseline. For the $\text{Cu}(\text{OH})_2$ nanowire modified glassy carbon electrode (GCE), $\text{Cu}(\text{OH})_2$ nanowires were carefully collected from the nanohybrid and then dispersed in 0.5 wt% Nafion solution. The bare GCE was polished with 500 nm alumina powders, followed by rinsing thoroughly with dehydrated alcohol and deionized water. After the GCE was cleaned up, 10 μL of the suspension containing $\text{Cu}(\text{OH})_2$ nanowires was dropped onto the GCE and then dried at room temperature. The electrochemical impedance spectroscopy (EIS) was collected from 10^5 to 0.01 Hz with an amplitude of 10 mV.

3. Results and discussion

3.1. Synthesis and characterization of the $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid

Fabrication strategy of the 3D hierarchical $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid is illustrated in Fig. 1A, which involves chemical dealloying of the $\text{Cu}_{60}\text{Zr}_{35}\text{Al}_5$ glassy precursor using 10 mM HF etching solution to produce free-standing NPC, followed by oxidation of the NPC thin film with an alkaline oxidative solution to grow $\text{Cu}(\text{OH})_2$ nanograsses onto the open nanoporosity. Typical structure features of the prepared NPC thin film show that the entire NPC sample has a uniform and bi-continuous nanoporous structure with a thickness of $\sim 1.2 \mu\text{m}$ and pore size of $\sim 50 \text{ nm}$ (Fig. S1). Fig. 1B exhibits the color change of the samples at different synthesis stages, i.e., from the silver shine for the $\text{Cu}_{60}\text{Zr}_{35}\text{Al}_5$ glassy precursor to the reddish-orange for the NPC and finally to the pale blue for the $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid. SEM observation of the resultant hybrid material shows that the surface of the NPC thin films is covered with dense and uniform $\text{Cu}(\text{OH})_2$ nanograsses (Fig. 1C).

The $\text{Cu}(\text{OH})_2$ NGA and NPC hybrids were synthesized through the alkaline oxidative method, wherein the morphology of the $\text{Cu}(\text{OH})_2$ nanograsses can be tailored by etching time. Due to the high surface area of the NPC substrate, the oxidation process can be accelerated drastically by introducing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaOH. The length and amount of the nanograsses evidently increases with the increasing etching time (Fig. S2). Fig. 2A and B show representative top-view and cross-sectional SEM images of the $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid at a constant reaction time of 120 s, respectively. As can be seen in Fig. 2A, the $\text{Cu}(\text{OH})_2$ nanograin grew from the pores of the NPC film, forming a lawn-like structure. Interestingly, multiple nanograsses often root on the same spot, like hair growing from follicles. The width of a single nanograin is about 100–200 nm (the inset in Fig. 2A). From Fig. 2B, it is clear that the nanohybrid possesses a hierarchically sandwich-like structure consisting of two outer layers of $\text{Cu}(\text{OH})_2$ NGAs grown on the NPC, giving rise to a large surface area ($\sim 38.2 \text{ m}^2 \text{ g}^{-1}$) of the $\text{Cu}(\text{OH})_2$ NGA@NPC hybrid (Fig. S3). Fig. 2C shows a TEM image of typical $\text{Cu}(\text{OH})_2$ nanograsses which have a needle-like shape and smooth surface. The corresponding selected area electron diffraction (SAED) pattern (Fig. 2D) indicates that the nanograin is the single crystal growing along the [100] direction on the (010) plane, as reported in literature (Wang et al., 2003; Wu et al., 2005; Zhang et al., 2003). It should be noted that $\text{Cu}(\text{OH})_2$ is very sensitive to electron beam irradiation and thus it is readily transformed to CuO by the focused high-energy electron beam. The diffraction ring shown in Fig. 2D is therefore attributed to the CuO nanocrystals produced by electron beam radiation damage to the $\text{Cu}(\text{OH})_2$. This point is further confirmed by TEM observations of the $\text{Cu}(\text{OH})_2$ nanograin for different electron beam radiation durations (Fig.

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