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Original Research

High reproducibility and sensitivity of bifacial copper nanowire array for detection of glucose☆

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ABSTRACT

The ordered bifacial copper nanowire array (Cu BNWA) was synthesized by a template assisted electrochemical deposition method. The morphology and structure of the as-prepared samples were investigated by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). The results show that the ordered Cu nanowire array with uniform geometrical dimensions covered both side of the Cu substrate. When used as the electrode for glucose detection, the minimum detectable concentration of glucose can be reached as low as 0.2 mM. Impressively, the sample still showed high sensitivity and stability for glucose detection after two months placement in ambient environment. These excellent performances of the Cu BNWA make it a promising non-enzyme glucose detection sensor for various applications.

1. Introduction

Accurate detection of glucose in human body provides critical insight into humongous scientific technological importance for clinical analysis of diabetes [1]. The traditional means for detecting glucose are focus on enzyme sensors due to the high sensitivity. With the increasingly demanding of glucose monitors, the utilization of enzyme-based sensors are gradually replaced by the stable sensitive non-enzymatic sensors owing to the high stability, high reproducibility and anti-interference [2]. Among all non-enzymatic glucose detection materials, the well aligned nanowire array is outstanding attributed to the uniform array structure, which not only acts out the superior electronic collection feature to alleviate the level of signal-to-noise, but also offers a jarless environment for the exchange of substances [3].

Comparing to the traditional nanostructure materials, matrix structure three-dimensional nanoarray shows more special holistic effect existed in the single nanowires, which contributes to strengthen these macroscopic properties [4]. Much efforts have been made on the utilization of three-dimensional nanoarray materials owing to the special uniform structure in nano level that offers them more potential properties in macroscopic structure, such as optical [5,6], energy [7], electronic [8] and chemical sensors [9–11]. To date, many different methods have been used for the preparation of nanowire array, such as hydrothermal [12,13],etching [9] and template assisted methods [3,14]. Templated based synthesis provides robust ways of precise control over the size, shape and configuration, and growth direction and place of otherwise unattainable nanostructured materials [14].

As a non-enzymatic glucose detection nanomaterial, Cu-based nanowire array has attracted much attention because of the easy availability, high electrical conductivity and extremely low price relative to the precious metal detector. Most of the glucose sensor nanowire array materials are formed on one side of the as-prepared conducting substrate or on the surface of substrate that prepared in former deposition [3,15]. The structure with a single face has achieved the uniformly spread of nanowires on one side of the supporting substrate, but the other side is always sealed while working as the monitor electrode of glucose. To overcome this drawback in utilization as glucose sensor and improve the sensitivity of the detection electrode, we present a simple strategy to make a bifacial detection electrode that makes full use of double faces of the sensor. The regularity of the bifacial nanowires offers the material a solid internal structure ensuring the stability of the application, it also supplies a larger surface area for the contact between glucose and the detection electrode to enhance the sensitivity as a sensor.

In this study, the copper bifacial nanowire array has been fabricated synchronously by a simple polycarbonate (PC) template assisted electrochemical deposition method. The as-prepared sample as a sensor electrode without further processing showed clearly response peak during the concentration of glucose solution low to 0.2 mM, which was much lower than the normal level of FBG (fasting blood glucose) and kept a stable response peak in CV after two months placement in ambient environment. The high sensitivity and reproducibility of the

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as-prepared Cu BNWA sensor electrode shows a promising usage in non-enzymatic glucose detection.

2. Experimental

2.1. Materials and reagents

Copper foil (99.99%, thickness ~500, 150 μm), PC template (diameter ~200 nm) were purchased from Whatman. Ethanol (C_2H_5OH), hydrochloric acid (HCl), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), ammonium sulfate ($(NH_4)_2SO_4$), diethylenetriamine (DETA), dichloromethane (CH_2Cl_2), sodium hydroxide (NaOH), and glucose ($C_6H_{12}O_6$) , were used as received without further purification.

2.2. Synthesis of Cu BNWAs

The synthesis process is shown in Fig. 1. Briefly, polished cathode Cu foil (150 μm), two pieces of PC templates, filter paper soaked with electrolyte, and another two thicker anode Cu foils (500 μm) were packed in sequence to form an electrochemical deposition device. Electrolyte components included $CuSO_4{\cdot}5H_2O$ (100 g L^{-1}), $(NH_4)_2SO_4$ (10 g L^{-1}) and diethylenetriamine (DETA, 40 ml L^{-1}). The deposition device was connected into the workstation (LK2005A) for the electrochemical deposition using a standard three-electrode system with Hg/Hg_2SO_4 as the reference electrode. The Cu BNWA was obtained at a scan rate of 3 mV s^{-1} in the potential range of −0.8 V to −1.0 V (vs. Hg/Hg_2SO_4) at room temperature. After deposition, the PC template was removed by immersing the samples in CH_2Cl_2 solution for 1 h. The

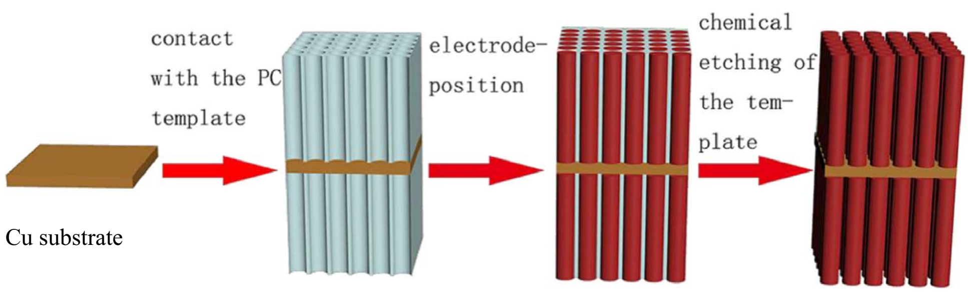

Fig. 1. Schematic diagrams showing the process of the template assisted electrochemical deposition of Cu bifacial nanowires array.

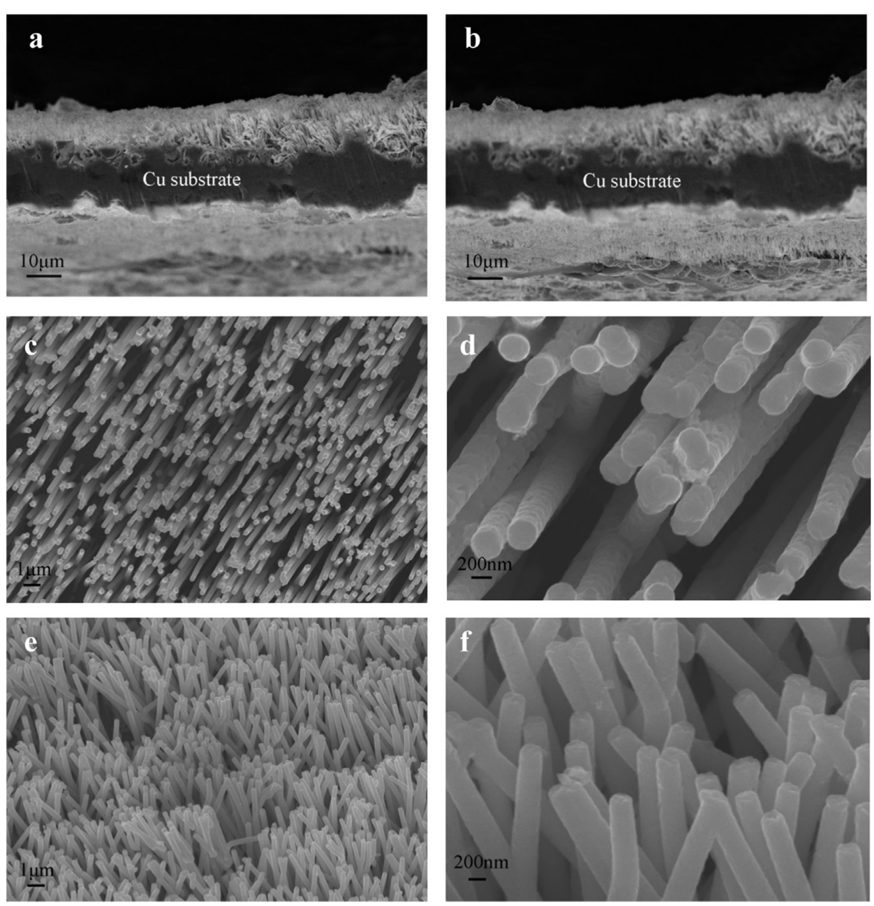

Fig. 2. FESEM images of the as-prepared Cu BNWA. **(a)** and **(b)** the Cu BNWA and Cu substrate, **(c)** and **(d)** Cu nanowire array on one side of Cu substrate, **(e)** and **(f)** Cu nanowire array on the other side of Cu substrate.