



Short Communication

Monolithically integrated copper phosphide nanowire: An efficient electrocatalyst for sensitive and selective nonenzymatic glucose detection

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ABSTRACT

The detection of glucose plays a significant role in diagnostics and management of diabetes and it is thus desired to develop non-noble-metal electrocatalyst for nonenzymatic glucose sensing. This work demonstrates the first use of monolithically integrated copper phosphide nanowire on copper foam (Cu₃P NW/CF) as an efficient catalyst for electrochemical oxidation of glucose. As a nonenzymatic glucose sensor, this Cu₃P NW/CF exhibits a low detection limit of 0.32 μM at a signal-to-noise ratio of 3 with a linear range from 0.005 to 1 mM (R² = 0.997). It also shows high anti-interference property to other normally co-existing electroactive species including lactose, fructose, ascorbic acid, uric acid, urea, dopamine, and sucrose as well as excellent resistance to chloride poisoning. Its application for glucose detection in human serum sample is also demonstrated successfully.

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1. Introduction

Fast and reliable glucose sensing is of critical importance in medical diagnosis, safety food production and environment screening [1]. The past decades have witnessed the use of many techniques for glucose determination, including fluorimetry [2], colorimetry [3–5], photoelectrochemistry [6], and electrochemistry [7–10], etc. Among them, electrochemical glucose sensing has received most intensive attention with advantages of simplicity, fast response, high sensitivity and suitability for real-time detection. Although glucose oxidase (GOx)-based amperometric biosensors have been widely used for sensitive and selective glucose detection, GOx suffers from high cost, insufficient long-term stability and complicated immobilization procedure. As such, it is highly attractive to develop nonenzymatic glucose sensors based on direct electrochemical oxidation of glucose.

So far, precious metal [11–14] and transition metal [15–21] based catalyst materials have been widely used as active electrocatalysts for nonenzymatic glucose sensing. Noble metals are too expensive, preventing their widespread use. Transition metal-

based catalysts also have two major drawbacks: (1) the formation of close-packed structures on electrode surface leading to decreased specific surface area and thus electrochemical performance; (2) the poor electronic conductivity. Obviously, monolithically integrated nanoarray catalysts have merits of structural stability, high surface area, more exposed active sites, and reduced catalyst usage without sacrificing catalytic performance. Such configuration is promising as an ideal catalyst electrode for nonenzymatic glucose detection.

Transition-metal phosphides (TMPs) represent an important class of compounds with metalloid characteristics and good electrical conductivity [22]. Our and other groups have recently demonstrated that they behave as efficient non-noble-metal catalysts for electrochemical water splitting [23–27]. In this communication, we describe the first use of monolithically integrated copper phosphide nanowire on copper foam (Cu₃P NW/CF) as an interesting catalyst for efficient electrochemical oxidation of glucose. Our results demonstrate that this 3D Cu₃P NW/CF exhibits greater performance with a limit of detection (LOD) of 0.32 μM at a signal-to-noise ratio of 3. It also shows favorable selectivity due to its high anti-interference property and excellent resistance to chloride poisoning.

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2. Experimental

2.1. Reagents and materials

Sodium hypophosphite (NaH_2PO_2), uric acid (UA), dopamine (DA), and urea were purchased from Aladdin Ltd. (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH), ammonium persulfate (APS), lactose (LA), glucose, ascorbic acid (AA), fructose, sucrose, and sodium chloride (NaCl) were purchased from Beijing Chemical Corporation. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

2.2. Preparation of Cu_3P NW/CF

Cu_3P NW/CF was prepared according to our previous reported method with some modifications [25]. CF was washed with diluted HCl and water several times to remove the surface oxide. To prepare $\text{Cu}(\text{OH})_2$ nanowire precursor on CF ($\text{Cu}(\text{OH})_2$ NW/CF) the cleaned CF was immediately immersed into a 30 mL solution (4 mmol APS and 80 mmol NaOH) at room temperature for 30 min. The CF was taken out of the solution and washed with de-ionized water several times and dried in air. The $\text{Cu}(\text{OH})_2$ NW/CF and NaH_2PO_2 (0.04 g) were placed at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the furnace. Subsequently, the sample was heated at 300°C for 2 h in Ar atmosphere, and then cooled to ambient temperature under Ar atmosphere to make Cu_3P NW/CF.

2.3. Characterization

Scanning electron microscopy (SEM) measurements were carried out on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 electron microscopy with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) data were collected on a RigakuD/MAX 2550 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including working electrode, counter electrode, and reference electrode.

2.4. Electrochemical measurements

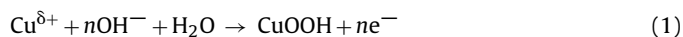
All electrochemical measurements were conducted in a typical three-electrode setup with an electrolyte solution of 0.1 M NaOH, using Cu_3P NW/CF as the working electrode, a platinum wire as the counter electrode and Ag/AgCl electrode as the reference electrode.

3. Results and discussion

Fig. 1a shows the XRD pattern of Cu_3P NW/CF in the diffraction angle range of $10\text{--}90^\circ$. The diffraction peaks are well indexed to Cu_3P (JCPDS No. 71-2261) and metallic Cu (JCPDS No. 03-1018) [25]. Fig. 1b shows the low-magnification SEM image of Cu_3P NW/CF. It is clearly seen that the entire surface of CF is completely wrapped by Cu_3P nanowire array. The high-magnification SEM image further reveals that such nanowires have rough surface with an average diameter of 250 nm, as shown in Fig. 1c. The TEM image suggests it consists of small nanoparticles (Fig. 1d). Fig. 1d inset presents the high-resolution TEM (HRTEM) image taken from one single nanowire and the well-resolved lattice fringes with an interplanar distance of 0.200 nm is corresponding to the (300) plane of Cu_3P [25].

We directly utilized Cu_3P NW/CF as a 3D electrode to test its electrocatalytic performance toward glucose electro-oxidation in 0.1 M NaOH. Bare CF and $\text{Cu}(\text{OH})_2$ NW/CF were also examined for comparison. Fig. 2a displays the cyclic voltammograms (CVs) of CF, $\text{Cu}(\text{OH})_2$ NW/CF, and Cu_3P NW/CF electrode in 0.1 M NaOH with and without the presence of 0.5 mM glucose at a scan rate of 30 mV s^{-1} . It is seen that although bare CF and $\text{Cu}(\text{OH})_2$ NW/CF are active for glucose electro-oxidation, the responses of them towards glucose are quite weak. In contrast, the Cu_3P NW/CF exhibits notable catalytic current density about 12 mA cm^{-2} at 0.42 V in the process of glucose oxidation. It is well worthy to note that the Cu_3P NW/CF presents no redox peak in the absence of glucose. We also studied the influence of Cu_3P nanowire length on electrocatalytic performance. It suggests that the use of a shorter reaction time of 10 min for precursor preparation leads to nanowire length of 10 μm (Fig. S1a), much shorter than that obtained with 30-min reaction time (20 μm) shown in Fig. S1b. Besides, shorter nanowire length gives lower catalytic current (Fig. S1c). All these observations indicate that Cu_3P NW/CF shows greatly enhanced catalytic activity which is strongly related with Cu_3P nanowire length.

To further investigate its sensing performance of Cu_3P NW/CF electrode toward nonenzymatic glucose detection, we examined the electrochemical behaviors of Cu_3P NW/CF toward different concentrations of glucose. Clearly, Cu_3P NW/CF electrode has no obvious anodic current peak in blank NaOH solution. With increasing concentration of glucose from 0 mM to 3.5 mM, an obvious oxidation process starts at approximate 0.25 V and reaches a peak at about 0.5 V, which could be attributed to the conversion of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{III})$ [28]. It has been reported that once an electrical potential was applied to electrode in NaOH solution, its surface underwent an electrochemical oxidation process [29,30]. The reaction equations of glucose oxidation process are described as follows [31,32]:



Hence, Cu_3P NW/CF could catalyze oxidation of glucose to generate gluconic acid and then reduced to the original $\text{Cu}(\text{II})$. The corresponding peak potential of glucose oxidation shift to positive may be attributed to the diffusion delay of glucose at the electrode surface [33]. Fig. 2c shows linear response of oxidation peaks around 0.5 V with correlation coefficient $R^2 = 0.993$ and a good linear relationship is obtained in the concentration range of 0.5–3.5 mM, which indicates that Cu_3P NW/CF electrode exhibits good electrocatalytic behaviour [34]. We further examined the amperometric responses to glucose of Cu_3P NW/CF at different pH values (Fig. S2). As observed, the current density increases with increased pH and it reaches the highest sensitivity when the pH is 13 ($11450 \mu\text{A mM}^{-1} \text{ cm}^{-2}$). Thus, we choose 13 as the optimal pH in our present study.

The effective surface area is essential to evaluate the electrocatalytic properties of electrode. To estimate the surface areas, we employ the capacitances of the double layer by CV method at the solid/liquid interface of both electrodes. Fig. 2d and e shows CV curves of the Cu_3P NW/CF and CF, which exhibit nearly rectangular shapes at different scan rates from 10 mV s^{-1} to 200 mV s^{-1} . It can be used as an approximate guide for surface roughness within an order-of-magnitude accuracy [35]. We collect the potential region of -0.255 V to -0.216 V , where the current density response should only be attributed to the charging of the double layer. Fig. 2f shows the capacitive currents at -0.235 V as a function of scan rate for Cu_3P NW/CF and CF ($\Delta j_0 = j_a - j_c$). The capacitance of Cu_3P NW/CF and CF is 4.048 mF cm^{-2} and 1.90 mF cm^{-2} , respectively, thus indicating Cu_3P NW/CF has a much higher surface roughness than CF, which could explain the much higher catalytic oxidation properties of Cu_3P NW/CF than CF.

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