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# Copper nanoparticle/graphene oxide/single wall carbon nanotube hybrid materials as electrochemical sensing platform for nonenzymatic glucose detection

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ABSTRACT

Cu nanoparticle/graphene oxide/single walled carbon nanotube (CuNP/GO/SWCNT) composites were prepared by a facile electrodeposition method and used for constructing nonenzymatic glucose sensor. Scanning electron microscopy (SEM) and Raman spectroscopy were employed to characterize the morphology and structures of the samples. The electrocatalytic performance of CuNP/GO/SWCNT composites towards glucose oxidation was studied by cyclic voltammetry (CV) and current–time measurements. Electrochemical results indicated that CuNP/GO/SWCNT electrode exhibited a higher electrocatalytic activity towards the oxidation of glucose than CuNP, CuNP/GO and CuNP/SWCNT electrodes. This was because the GO/SWCNT composite as substrate material not only possessed excellent conductivity, but also provided large surface area for the high loading of the CuNPs. Meanwhile, the good dispersibility, independent and multi-layer structure of CuNP, could enhance the charge-transport properties, and afford more active sites for the catalytic oxidation of glucose. Under the optimized conditions, the sensor showed a high sensitivity of up to 930.07 μA $mM^{-1}$ $cm^{-2}$, with a wide linear range of 1 μM to 4.538 mM and a low detection limit of 0.34 μM (S/N = 3). It also exhibited excellent stability, reproducibility, selectivity, and reliable measurement in real human blood samples. All of these excellent properties made the CuNP/GO/SWCNT composite material promising for the development of effective nonenzymatic glucose sensors.

## 1. Introduction

Glucose detection has attracted widespread attentions due to urgent requirements in food industry, fermentation industry, biochemistry, clinical diagnosis and environmental protection [1–5]. Therefore, it is necessary and urgent to develop a fast, remarkable sensitivity, high selectivity, reliable and stable technology to detect glucose levels. For a few decades, various glucose enzyme sensors based on the immobilization of glucose oxidase have been fabricated. However, enzyme based amperometric glucose sensors usually suffer from drawbacks, such as easily affected by temperature, pH value, and toxic chemicals [6–8] due to the inherent nature of enzymes. Moreover poor stability and high cost of enzymes limit their wide applications [9,10]. To overcome these obstacles, a direct electrocatalysis nonenzymatic glucose sensor is an attractive alternative technique which is free from the environmental conditions mentioned above.

It is known to all that electrode active materials are considered to be the determinant factor affecting the analytical properties of a nonenzymatic glucose sensor. Recently, a variety of noble metal nanomaterials, including Pt [11], Pd [12], Au [13] and Ag [14] nanomaterials have been employed as nonenzymatic glucose sensors. Though these sensor based noble metal nanomaterials showed good sensitivity and low detection limit, these sensors have some disadvantages, such as high cost, [15,16] poor stability, selectivity and low sensitivity [17].

In contrast, Cu-based materials as electrode active materials have several genuine advantages. They have lower price compared with most noble metals. Moreover, the Cu-based materials could promote electron transfer reactions and possess good electrochemical activity. [18,19] Up to now, many sensors based on different Cu-based materials have been made for the detection of glucose. For instance, Ni et al. [15] developed a nonenzymatic amperometric glucose sensor via the Cu nanoparticles (CuNPs) onto the electrodeposited poly(3,4-ethylenedioxythiophene)/graphene oxide (GO) nanocomposite film. The corresponding sensitivity was 909.1 μA $mM^{-1}$ $cm^{-2}$, and the liner range was from 0.1 μM to 1.3 mM. Wang et al. [20] prepared the reduced GO/CuNP nanocomposites by simultaneous reduction/deposition

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method on a glass/Ti/Au electrode for nonenzymatic glucose sensor. The liner range was up to 1.2 mM and the sensitivity was 447.65 μA mM$^{-1}$ cm$^{-2}$. Kong et al. [21] prepared a hollow CuO polyhedron-modified electrode by a templating approach for the fabrication of nonenzymatic glucose sensor, and it showed a liner range up to 4 mM with a sensitivity of 1112 μA mM$^{-1}$ cm$^{-2}$. These above-mentioned Cu-based materials sensors showed high sensitivity and wide liner range for glucose detection, indicating Cu-based materials possessed excellent electrocatalytic activity towards the oxidation of glucose.

For the fabrication of glucose nonenzymatic sensors with nanomaterials, the preparation and control of particle size and their morphology are critical as they exert significant effects on the properties of these materials. It is well-known the substrate materials have important influence on the size and morphology of particles. Hence, the substrate of an electrode is very significant at the process of building a nonenzymatic glucose sensor [22,23]. Recently, graphene and carbon nanotubes (CNTs) captured enormous popularity because of their unique properties, such as low noise level property, high conductivity and charge carrier mobility during the catalytic reactions, and large specific surface areas [24–26]. Unfortunately, there are some shortcomings when the pure graphene or CNTs are used as substrate materials. Both the CNTs and graphene easily precipitate irreversibly due to π–π interactions and van der Waals interaction, which makes them difficult to disperse in most of solvents and increases the difficulty in application [27,28]. In order to solve this problem, several research groups provided feasible solutions and made excellent achievements [29–31]. They demonstrated that GO could absorb on the CNTs through the strong π–π interaction, where GO served as a superior dispersant to disperse CNTs and prevented their aggregation. The GO/CNT composite displayed enhanced electronic and catalytic activity, which could be used for construction of electrochemical sensors with better performances.

In this study, graphene oxide/single wall carbon nanotube (GO/SWCNT) composites were prepared by sonication method, and CuNPs were further loaded on GO/SWCNT composite by electrodeposition approach. The GO/SWCNT composite as a substrate material not only provided large specific surface area for the high dispersion of CuNPs, but also enhanced the conductivity, which can facilitate the electron transfer during the catalytic reactions. Meanwhile, the good dispersibility and multi-layer structure of spherical CuNPs could improve the charge-transport properties, and afford more active sites for the catalytic oxidation of glucose. Under optimal conditions, this nonenzymatic glucose sensor exhibited a high sensitivity up to 930.07 μA mM$^{-1}$ cm$^{-2}$, a wide linear range from 1 μM to 4.538 mM, and a low detection limit of 0.34 μM for glucose oxidation. Moreover, the prepared electrode displayed a good selectivity, high stability and good repeatability. The practical application of CuNPs/GO/SWCNTs/GCE was tested by determining the glucose concentration in human blood samples.

## 2. Experimental

### 2.1. Materials and apparatus

Graphene oxide and single walled carbon nanotubes were purchased from Nanjing Xian Feng Nanomaterials Technology Co., LTD. (Nanjing, China). D-(+)-glucose, ascorbic acid (AA), uric acid (UA) and dopamine (DA) were purchased from Aladdin Chemistry Co., LTD. Sodium hydroxide (NaOH), copper (II) sulfate anhydrous ($CuSO_4$) and sodium sulfate anhydrous ($Na_2SO_4$) were purchased from Xilong Chemical Co., LTD. All reagents were analytical grade and used without further purification. All solutions were prepared using deionized distilled water.

The morphology of the nanocomposites was characterized by a scanning electron microscope (SEM, Hitachi S-3000 N). Raman spectroscopy (Renishaw in via 2000) was used to analyze the samples using a 514 nm Ar laser. All electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai, China) using a three electrode system: the modified glassy carbon electrode (GCE) ($\Phi = 3$ mm), platinum wire and saturated calomel electrode (SCE) as working, counter, and reference electrode, respectively. All potential values given below referred to SCE.

### 2.2. Fabrication of GO/SWCNT composites

GO/SWCNT composites were prepared by a sonicate procedure. In a typical synthesis, GO (1.0 mg) was dispersed into 5.0 mL doubly distilled water and sonicated for 1 h to yield a yellow-brown dispersion. Then 0.5 mg of SWCNT was added into the homogeneous GO dispersion and sonicated until a homogeneous black suspension was obtained. In GO/SWCNT suspension, the concentrations of GO and SWCNTs were 0.2 mg/mL and 0.1 mg/mL, respectively.

### 2.3. Preparation of the CuNP/GO/SWCNT composite modified electrode

Prior to coating, the glassy carbon electrodes were carefully polished with 0.05 mm $Al_2O_3$ powders, followed by thorough rinsing with deionized water. After sequential ultrasonically cleaned with deionized water, absolute ethanol and deionized water each for 5 min, the electrodes were dried at room temperature. 6 μL of the GO-SWCNT nanocomposite suspension was dropped on the surface of cleared GCE and dried at room temperature. Then the GO/SWCNT composite modified electrode was immersed in a solution containing 10 mM $CuSO_4$ and 100 mM $Na_2SO_4$ and electrodeposition was carried out at a potential of $-1.0$ V (vs. SCE) for 300 s. For the comparison, CuNPs/GO/GCE, CuNPs/SWCNTs/GCE and CuNPs/GCE were also fabricated in a similar method.

### 2.4. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) were measured in 5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) mixture with 0.1 M KCl in the frequency range of 0.1 to 10,000 Hz. The amplitude of the applied sine was 5 mV with the current potential set as 0.2 V. The electrochemical measurements for glucose oxidation at the CuNPs/GO/SWCNTs/GCE were performed in a 0.1 M NaOH solution. Amperometric curves were obtained after adding a desired concentration of glucose under constant stirring. All the measurements were carried out at room temperature.

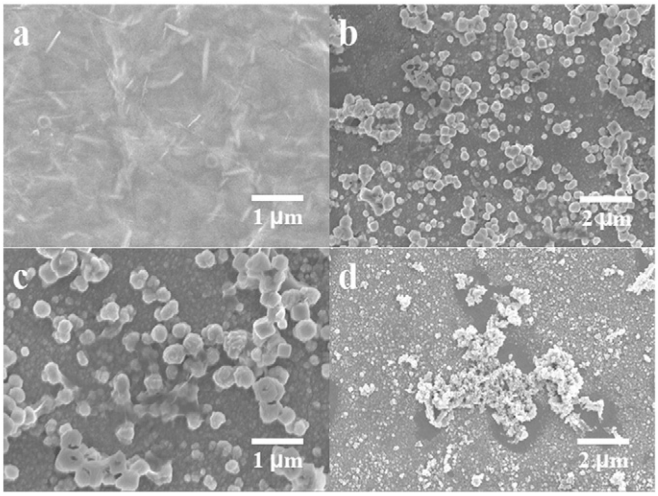

**Fig. 1.** Scanning electron microscope images of GO/SWCNT (a), CuNP/GO/SWCNT low (b) and high (c) magnifications and CuNP (d). Deposition potential: -1.0 V vs. SCE, deposition time: 300 s.