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Short communication

# Fixure-reduce method for the synthesis of $Cu_2O$/MWCNTs nanocomposites and its application as enzyme-free glucose sensor

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ABSTRACT

$Cu_2O$/MWCNT (multi-walled carbon nanotubes) nanocomposites were successfully prepared in large quantities with a new fixure-reduction method under low temperature. The morphology and shape of the $Cu_2O$/MWCNTs nanocomposites were characterized by field emission scanning electron microscopes (FESEMs), energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD), respectively. Cyclic voltammetry (CV) was used to evaluate the electrochemical performance of the $Cu_2O$/MWCNTs nanocomposites modified electrode towards glucose. Compared to the bare GCE, the $Cu_2O$ nanoparticles and the MWCNTs modified electrode, the $Cu_2O$/MWCNTs modified electrode displays high electrocatalytic activity towards the oxidation of glucose. With a potential of −0.20 V, the $Cu_2O$/MWCNTs modified electrode was used to determine glucose by amperometric, showing significantly lower overvoltage and a linear dependence ($R$ = 0.9958) in the concentration up to 10 μM with a sensitivity of 6.53 μA μmol $L^{-1}$ and a detection limit of 0.05 μmol $L^{-1}$ (signal-to-noise ratio of 3). In summary, the preparation process of the nanocomposites is very simple and the nanocomposites could be used for the development of enzyme-free glucose sensor.



## 1. Introduction

Due to the special structure, the extraordinary mechanical and unique electronic properties and the potential applications, carbon nanotubes (CNTs) have attracted considerable attention since they were discovered (Iijima, 1991; Musameh et al., 2002). Recent studies of CNTs have focused on depositing metal or metal oxide nanoparticles onto the nanotube's surface (Ionescu et al., 2008; Chen et al., 2008; Chen and Lu, 2008; Gu and Wong, 2006). The physical and chemical properties of nanotube deposited nanoparticles may be changed to obtain desired properties. Currently, copper and his oxide have shown to be excellent amperometric sensors over a wide range of concentrations (Batchelor et al., 2008; Zhuang et al., 2008; Zhang et al., 2008). It is expected that $Cu_2O$ and CNT hybrid nanostructures can be used to build amperometric sensors, owing to their greater ability to promote electron-transfer reactions and large surface area. There are several methods reported for the synthesis of $Cu_2O$/MWCNTs nanocomposites (Yu et al., 2005; Li et al., 2006; Wang et al., 2007). However, these methods are complicated, high cost and low yield. Furthermore, the mechanism of $Cu_2O$ nanoparticles growing on the surface of MWCNTs was not discussed, which is very important in the controlling of conditions in a synthesis process. Therefore, a facile and cheap method for the large scale synthesis of uniform $Cu_2O$/MWCNTs nanocomposites and the discussion of the possible mechanism are necessary.

At the same time, because of the great importance of sugar sensing in human blood, which may help diabetic people, who constitute about 5% of the world's population (Heller and Feldman, 2008), the electrocatalytic oxidation of glucose has been a focal subject of many investigations (Wang, 2008; Clark et al., 1962; Reach and Wilson, 1992; Turner et al., 1999; Katz et al., 1999; Mano et al., 2003). Amperometric enzyme electrodes, based on glucose oxidase (GOx), have played a leading role in the move to simple easy-to-use blood sugar testing and are expected to play a similar role in the move toward continuous glucose monitoring (Heller, 1990; Liaudet et al., 1990; Badia et al., 1993).

Good selectivity and high sensitivity have been achieved for glucose detection by such enzymatic sensors, however, owing to the nature of enzymes, the most common and serious problem with enzymatic glucose sensors lies in their lack of long-term stability. To solve this problem, nonenzymatic glucose sensors have also been explored in the hope of improving the electrocatalytic activity and selectivity towards the oxidation of glucose. Early researches have focused on the use of noble metals Pt and Au for develop-

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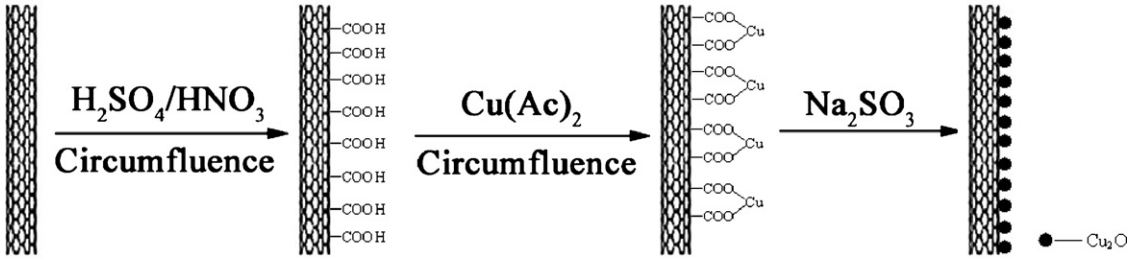


**Scheme 1.** Schematic procedure for the preparation of $Cu_2O$ nanoparticles on MWCNTs surface.

ing enzyme-free sensors (Vassilyev et al., 1985; Azdic et al., 1989; Beden et al., 1996; Hsiao et al., 1996). However, these electrodes often have drawbacks of low sensitivity and poor stability caused by surface poisoning from the adsorbed intermediates (Ernst et al., 1979; Bae et al., 1991).

In this work, $Cu_2O$/MWCNTs nanocomposites were successfully prepared in large quantities with a new fixure-reduction method under low temperature. The prepared materials integrated the merit of electron transfer of MWCNT with electrochemical activity from $Cu_2O$ and were successfully applied as an enzyme-free glucose sensor. By comparison, the electrochemical catalytic activity of the sensor toward glucose oxidation is better than that of the $Cu_2O$ nanoparticles and MWCNTs individual.

## 2. Experimental

### 2.1. Chemicals

MWCNTs (>50 nm diameter, 0.5–1 μm length and >95% purity) were obtained from Institute of Chinese Academy of Science (China). Cuprous acetic, $KH_2PO_4$, $Na_2SO_3$, and $K_3[Fe(CN)_6]$ were obtained from Shanghai Chemical Corp (China). D(+)-Glucose (97%) and Nafion (5 wt.%) were purchased from Sigma–Aldrich. All other reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with doubly distilled water.

### 2.2. Synthetic procedures

MWCNTs were chemically shortened by ultrasonic agitation in a mixture of sulfuric acid and nitric acid (3:1) for about 8 h. The resulting MWCNTs were separated and washed with distilled water by centrifugation (4000 rpm) until the pH of the resulting MWCNTs solution became neutral. The resulting MWCNTs were dispersed in the 0.1 mol $L^{-1}$ $Cu(Ac)_2$ about 2 h under ultrasonic agitation. And then, 0.2 g $Na_2SO_3$ were added to the mixture with vigorously stirring to homogeneity and then transferred into a 60 mL steel autoclave. The clave was sealed, maintained at 80 °C for 2 h and then cooled naturally to the room temperature. The product was washed with distilled water and ethanol for several times to remove the impurities before characterizations.

### 2.3. Electrochemical measurements

The modified electrode was prepared as follows: GC electrodes (3 mm diameter) were carefully polished with a diamond pad/3 μm polishing suspension, rinsed with distilled water and ethanol, and then dried under ambient nitrogen gas. $Cu_2O$/MWCNTs nanocomposites (10 mg) were dissolved in a mixture of 0.1 mL of Nafion perfluorosulfonated ion-exchange resin and 0.9 mL of distilled water. Approximately 60 min of ultrasonication was necessary to obtain uniformly dispersed $Cu_2O$/MWCNTs nanocomposites. After dropping 10 μL of the $Cu_2O$/MWCNTs nanocomposites solution onto the electrode surface, the electrode was dried in air. Electrochemical measurements were performed on a model CHI660B electrochemical analyzer (ChenHua Instruments Co. Ltd., Shanghai, China) controlled by a personal computer. Using the modified GC working electrode, the CV and CA data were measured in a mixture of 1 mmol $L^{-1}$ glucose and 20 mmol $L^{-1}$ phosphate buffer solution (PBS, pH 9.2). The CA measurements required operation of the electrode at a constant applied potential of −0.20 V versus SCE. Once the current reached a baseline in the absence of glucose, glucose was added every 40 s thereafter. The CV and CA measurements were carried out in 50 mmol $L^{-1}$ PBS (pH 9.2) under ambient air.

### 2.4. Characterization

XRD patterns of the products were recorded on a Shimadzu XRD-6000 X-ray diffractometer at a scanning rate of 0.05° $s^{-1}$ with a 2$\theta$ range from 10° to 80°, with high-intensity Cu Kα radiation ($\lambda$ = 0.154178 nm). Field emission scanning electron microscopes and energy dispersive X-ray analyses were obtained by JEOL JSM-6700 FESEM (operating at 10 kV). The HRTEM analysis used a JEOL 2010 instrument with an accelerating voltage of 200 kV.

## 3. Results and discussion

Scheme 1 shows the stepwise fabrication process of the $Cu_2O$/MWCNTs nanocomposite with a fixure-reduction method. First, MWCNTs were chemically acidified by circumfluence agitation in a mixture of sulfuric acid and nitric acid (3:1). Second, copper ions were fixed onto the surface of MWCNTs by chemical adsorption and physical adsorption (Fig. S1). Third, the copper ions fixed on the surface of the MWCNTs were reduced. And then, the $Cu_2O$/MWCNTs nanocomposites were synthesized.

Fig. S2a shows the XRD pattern of the MWCNTs (curve 1) and as-prepared $Cu_2O$/MWCNTs composites (curve 2), respectively. The peak at 2$\theta$ = 25.96° corresponds to the plane of (0 0 2) of graphite of MWCNTs (curve a) (Chen et al., 2003). And as shown in curve 2, there are four peaks with 2$\theta$ values of 36.52°, 42.44°, 61.54°, and 73.70° corresponding to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystal planes of pure $Cu_2O$ with cubic phase (JCDS 75-1531), respectively. From the XRD pattern, it can be concluded that the obtained $Cu_2O$/MWCNTs composites are composed of cubic $Cu_2O$ and MWCNTs. And according to the Debye–Scherrer equation, the average crystalline diameter of the obtained $Cu_2O$ particles is about 12.7 nm.

While Fig. S2b, showing the Cu 2p1/2 core level spectrum illustrates that the observed value of the binding energies for Cu 2p3/2 and Cu 2p1/2 are in agreement with the literature values of bulk for $Cu^+$ (Wang et al., 2003). Besides, the Cu 2p3/2 satellite peaks characterizing $Cu^{2+}$, usually centered at about 942 eV, are not found. And the result is the same as that of the XRD analysis, which means our sample is $Cu_2O$/MWCNTs nanocomposites. The prepared $Cu_2O$/MWCNTs composites were also investigated by FESEM. Fig. 1a and b shows some typical FESEM images of the $Cu_2O$/MWCNTs composites. A HRTEM micrograph (Fig. 1c)