



# Electrochemical synthesis of mixed-valence manganese/copper hybrid composite using graphene oxide and multi-walled carbon nanotubes for nonenzymatic glucose sensor



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## ABSTRACT

Electrochemical synthesis of mixed-valence manganese/copper hybrid composite has been successfully performed using graphene oxide (GO) and multi-walled carbon nanotubes (MWCNT) as a conductive and steric hybrid nanotemplate. The MnCu/MWCNT/GO hybrid composite shows compact and nanoporous structure due to high conductivity and high specific surface of the MWCNT/GO nanotemplate. XRD result indicates a mixed-valence hybrid composite including copper manganese oxide ( $\text{CuMn}_2\text{O}_4$ ), tenorite (CuO), and hausmannite ( $\text{Mn}_3\text{O}_4$ ). It is electroactive, pH-dependent, and stable in the electrochemical system. It shows electrocatalytic activity to glucose oxidation with high current response and low overpotential by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV). Particularly, DPV shows lower oxidation peak potential ( $E_{pa} = -0.05$  V) due to suitable control of pulse parameters. CV, LSV, and DPV response of MnCu/MWCNT/GO shows linear correlation between current response and glucose concentration estimated with sensitivity of 49.1, 58.6, and 59.3  $\mu\text{A mM}^{-1} \text{cm}^{-2}$ , respectively. It shows linear concentration range of 1–32 mM with a detection limit of  $1 \times 10^{-6}$  M ( $S/N \geq 3$ ). Coimmobilization and activity of manganese/copper hybrid composite can be effectively enhanced by MWCNT/GO. The MnCu/MWCNT/GO sensor shows high recovery and low coefficient of variation in bovine serum albumin samples for nonenzymatic glucose sensor.

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## 1. Introduction

Regular measurements of blood glucose levels are required to determine whether the treatments are working effectively for diabetic patients [1]. Enzyme-modified electrodes have some disadvantages, such as instability, the high cost of enzymes, complicated immobilisation procedures, and critical operating conditions. Therefore, considerable attention had been paid to developing nonenzymatic electrodes to overcome these problems. The direct electrocatalytic oxidation of glucose at a nonenzymatic electrode would have advantages over enzymatic electrodes. Recently, efforts to develop a practical nonenzymatic glucose sensor have been centred on achieving a breakthrough in electrocatalysis. In this context, different substrates, such as platinum [2], gold [3], copper [4], alloys (containing Pt, Pb, Au, Pd, Ir, and Ru) [5–8], and metal oxides ( $\text{IrO}_2$ ,  $\text{MnO}_2$ , and CuO) [9–11], have been studied. The most important finding in this area to date is that

the highly active surface area of the electrode material plays a key role in the electrooxidation of glucose.

During recent years, nanomaterials, such as carbon nanotubes (CNTs) and transition metallic nanoparticles (NPs), have been widely applied in sensors and biosensors. CNTs are an attractive material for electroanalysis due to their high surface/volume ratio and chemical stability [12–15]. Transition metallic NPs, including gold (Au), platinum (Pt), palladium (Pd), copper (Cu), nickel (Ni), and silver (Ag), can be used to increase electrochemical activities. Sensors and biosensors modified with metallic NPs have demonstrated good performances due to their increased surface area and enhanced mass transport and catalysis as well as good biocompatibility, with control over the microenvironment, relative to macroelectrodes [15–17]. Therefore, their use has been an important strategy in the construction of glucose nonenzymatic sensors with nanomaterials, such as nanoporous Pt electrodes [18,19] and electrodes modified with CNTs [20,21], Ni NPs [22], Au NPs [23,24], Cu NPs [25,26], CNTs with Cu NPs [27,28], and CNTs with Ni and Cu NPs [29].

Graphene oxide (GO) consists of a single atomic layer of  $\text{sp}^2$ -hybridized carbon atoms functionalized with mainly phenol,

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hydroxyl, and epoxide groups on the basal plane and ionizable carboxyl groups at the edges; it is obtained after treating graphite with strong oxidizers. GO can form stable single-layer aqueous dispersions due to the charge repulsion of the ionized edge acid groups. As a derivatized graphite nanomaterial, GO features a highly hydrophobic surface with non-oxidized polyaromatic nanographene domains on the basal plane. The abundance of highly conjugated structures on the surface of GO allows it to adhere readily to conjugated materials through  $\pi$ - $\pi$  interactions, making GO function as a unique tethered 2D surfactant sheet [30–35]. Recently, many studies have confirmed that GO is a good candidate for use as an advanced carbon material in electrochemical applications [36–38]. Because CNTs and GO exhibit many similar properties, while being structurally dissimilar, then on covalent preparation of rGO/CNT composites provides attractive building blocks for the development of nanocarbon materials with potentially improved conductivity and catalytic ability for electrochemical research.

High sensitivity and fast amperometric detection of glucose had been reported using the methods mentioned above due to an increase in the electrocatalytic active area and the promotion of electron transfer in glucose oxidation reactions. However, it's complicated for a directly and widely used screen printed carbon electrode in the practical applications due to the difficulty of electrode rotation in the pre-study by amperometry. In order to overcome this issue, we present a study focused on the electrochemical synthesis of manganese/copper hybrid composite using CNTs and GO by different electrochemical techniques, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV), respectively.

In the present work, the facile electrocatalytic oxidation of glucose was demonstrated by the MnCu/MWCNT/GO hybrid nanocomposites. Manganese acetate and copper sulphate were used to prepare manganese/copper hybrid composite on a MWCNT/GO-modified electrode by electrochemical synthesis. The mixed-valence nanoporous composite was studied by XRD and SEM. The electrocatalytic properties of MnCu/MWCNT/GO for glucose oxidation was investigated and compared with other modifiers including GO, MnCu, and MnCu/GO. The composite modified screen printed carbon electrode (SPCE) was also used to determine glucose in bovine serum albumin (BSA) samples.

## 2. Experimental

### 2.1. Reagents and materials

Glucose, manganese acetate, copper sulphate, and multi-walled carbon nanotubes (MWCNT) were purchased from Sigma–Aldrich (USA) and were used as-received. All other chemicals (Merck) used were of analytical grade (99%). Double-distilled deionized water ( $>18.1 \text{ M}\Omega \text{ cm}^{-1}$ ) was used to prepare all the solutions. All other reagents were of analytical grade and used without further purification. A pH 5.5 acetic solution was prepared with 0.1 M sodium acetate and adjusted to pH 5.5 by acetic acid.

### 2.2. Apparatus and measurements

The MnCu/MWCNT/GO hybrid composite was characterized by cyclic voltammetry (CV), SEM, linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV). A glassy carbon electrode (GCE) purchased from Bioanalytical Systems (BAS) Inc., USA. A screen printed carbon electrode (SPCE) was purchased from Zensor Inc., TW. All GCEs and SPCEs were used with diameter of 0.3 cm (exposed geometric surface area of  $A = 0.0707 \text{ cm}^2$ ) for all electrochemical techniques. Electrochemical experiments were

completed by a CHI 1205a electrochemical workstation (CH Instruments, USA) with a conventional three-electrode setup containing a GCE or a SPCE (working electrode), an Ag/AgCl (3 M KCl) (reference electrode), and a platinum wire (counter electrode). The buffer solution was entirely deaerated using nitrogen gas atmosphere. The morphological characterization of composite films was examined by means of SEM (S-3000H, Hitachi). Indium tin oxide (ITO) substrates were used in morphological and composite analysis for convenience.

### 2.3. Preparation of manganese/copper hybrid composite using MWCNT and graphene oxide

The electrodeposition of manganese/copper hybrid composite was carried out in pH 5.5 acetic solution containing 0.2 M manganese acetate and 0.1 M copper sulphate by consecutive cyclic voltammetry. Potential cycling was controlled in the potential range of  $-0.6$  to  $+0.6 \text{ V}$  with scan rate of  $0.1 \text{ V s}^{-1}$  and 20 scan cycles. Bare, GO, and MWCNT/GO modified electrodes were used to study the electrodeposition of manganese/copper hybrid composite. These modifiers were noted as “MnCu”, “MnCu/GO”, and “MnCu/MWCNT/GO”, respectively.

The MWCNT/GO modified electrode was prepared by two steps: firstly, the electrochemical reduction of graphene oxide (GO), then, the adsorption of MWCNT. The electrochemical reduction of graphene oxide was carried out in 0.5 M sulphuric acid containing  $0.5 \text{ mg ml}^{-1}$  GO solution. It was achieved by employing consecutive cyclic voltammetry in the potential range of  $-0.5$  to  $-1.2 \text{ V}$  (15 scan cycles, scan rate =  $0.05 \text{ V s}^{-1}$ ). All MWCNT were carboxylic-functionalized and well-dispersed in double distillation-deionized water ( $1 \text{ mg ml}^{-1}$ ) with sonication for 10 min before using [39]. By drop casting method,  $10 \mu\text{l}$  of the MWCNT solution was dropped on electrode surface and dried out in the oven at  $40^\circ\text{C}$ . After this procedure, it was mentioned as “MWCNT/GO” modified electrode for convenience. It was used to have the electrodeposition of manganese/copper hybrid composite as aforementioned. After these procedures, the “MnCu”, “MnCu/GO”, and “MnCu/MWCNT/GO” modified electrodes were prepared to study.

## 3. Results and discussion

### 3.1. Preparation and characterization of MnCu/MWCNT/GO hybrid composite

The electrodeposition of manganese/copper hybrid composite was studied with bare, GO, and MWCNT modified glassy carbon electrode (GCE) by consecutive cyclic voltammetry. Generally, electrodeposition of different metal ions (Mn and Cu ions) might suffer the competition problem resulted in poor electrodeposition. Fig. 1A shows the voltammogram of manganese/copper hybrid composite electrodeposition using a bare GCE. In the first scan segment (negative scan), it shows two significant cathodic peaks related to the electroreduction of Mn and Cu ions, respectively. In the second scan segment (positive scan), it shows two anodic peaks corresponded to the oxidation of manganese/copper hybrid composite. However, both cathodic and anodic peak currents are decreasing as increasing the scan cycles. By potential cycling, current decreases at redox peaks might indicate that the electrodeposition of manganese/copper hybrid composite is not perfect. In our strategy, GO and MWCNT/GO were used as conductive nanotemplates to enhance the hybrid electrodeposition of different metal ions (Mn and Cu ions). Inset of Fig. 1B shows the electroreduction of graphene oxide. All modified electrodes prepared by this procedure were called GO-modified electrodes. Fig. 1B and C shows the voltammograms of manganese/copper electrodeposition using a

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