Potentiodynamic Bottom-Up Growth of Cu/MnO_2 Composite Films as Glucose Sensing Electrode

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Abstract

Copper/manganese dioxide (Cu/MnO_2) composite films were developed on indium doped tin oxide (ITO) coated glass substrates by layer-by-layer electrochemical deposition under potentiodynamic mode for glucose sensor application. Surface morphology of Cu/MnO_2 composite films together with pristine MnO_2 and Cu films as reference was examined by optical microscopy and atomic force microscopy. The Cu particle-like clusters are evenly covered on underlying MnO_2 forming a bi-layered structure. The present work mainly investigates the performance of composite Cu/MnO_2 electrode towards glucose detection using amperometric measurement. Electrochemical experiments showed that the Cu/MnO_2 exhibited higher catalytic capability for glucose oxidation than pristine MnO_2 and Cu indicating that composition of Cu with MnO_2 causes a synergistic effect for glucose oxidation on the electrode surface. The electroactive surface area for glucose sensing estimated from Randles-Seveik relation is larger for Cu/MnO_2 electrode. A linear correlation of oxidation peak current densities of Cu/MnO_2 electrode to glucose concentration (0.25 – 1.25 mM) indicated that the sensitivity is as high as 0.67 mA mM^{-1} and detection limit is as low as 0.25 mM. The composite Cu/MnO_2 electrodes bear a promising potential for glucose sensor application.

KEYWORDS: Cu/MnO_2 composite electrode; Potentiodynamic deposition; Glucose sensor; Sensitivity; Detection limit

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Introduction

Glucose sensors have been extensively developed because of their broad applications, especially in diabetes diagnosis. A number of studies have been conducted over many years in developing glucose oxidase (GOx)-based enzymatic biosensors on account of high selectivity, good reliability [1 – 4]. Despite having much progress has been made in achieving better performance of electrochemical enzymatic glucose sensors, there are still some considerable challenges in order to negate their practical limitations such as high fabrication cost and poor stability, high complexity and poor reproducibility [5 – 10]. Non-enzymatic glucose sensors have drawn a great research interest due to their low cost, high stability, low detection limit and so on. Semiconducting metal oxides such as ZnO, ZrO_2 and MnO_2 have gained attention as electrode materials in non-enzymatic glucose sensors [11 – 16]. In addition, the nanotechnology development offers great opportunities for constructing nanostructured electrodes facilitating the larger surface area, better catalytic activities, chemical stability and fabrication flexibility for real world applications [17 – 18].

Manganese dioxide (MnO_2) is one of the most attractive inorganic materials and has been used in catalysis, molecular adsorption, energy storage and biosensors. In addition to its catalytic activity, it also renders the economic and environmental advantages. Despite having such advantages, their selectivity to glucose detection has not yet reached a satisfactory level. To address this issue, nanocomposition, coating noble metals (Cu, Ni etc.) on metal oxides, is a well-recognized strategy which could improve the properties of electrochemical sensors due to their synergistic effect. Some prior works reveal that the nanocomposites of metal and metal oxide can give a synergistic effect for glucose oxidation. Among the metals, Ni, Cu, Pb and Ag

are known to have good electron transfer for oxidation of glucose. In particular, copper (Cu) has been studied instead of enzyme for biosensor for the electrocatalytical glucose oxidation due to its electrical and catalytical properties. In the prior reports [19 – 22], the Cu/MnO_2 and Ni/MnO_2 composite electrodes were prepared from a solution containing precursor and reducing agent and the composites exhibited higher electrochemical currents and better catalytic activity.

In the present work, the Cu/MnO_2 composite was prepared by electrochemical deposition method where only precursor solution was used without the help of the reducing agent. Exclusion of reducing agent during deposition is the one different from the prior works where the reducing agent usually involves. The layer-by-layer deposition method was used to composite Cu and MnO_2 since it can endow the nanocomposite with multifunctional properties. A non-enzymatic glucose sensor based on Cu/MnO_2 composite was proposed and its electrochemical behaviors were studied in the present work. The composite Cu/MnO_2 electrode exhibits high sensitivity, low detection limit and moderate linear range towards the detection of glucose.

Materials and Methods

The Cu/MnO_2 composite films was prepared by the layer-by-layer electrodeposition technique using the electrochemical workstation (Corr Test: CS350). A schematic of electrodeposition process and the photographs of MnO_2 and Cu/MnO_2 composite samples are shown in Fig. 1. The indium-doped tin oxide (ITO)-coated glass substrates with the area of 1 cm^2 were cleaned by ultrasonication in detergents, acetone, ethanol and isopropyl alcohol (IPA) subsequently and each cleaning process took 10 minutes. Potassium permanganate ($KMnO_4$) and copper (II) sulphate ($CuSO_4$) were separately prepared in 50 ml of deionized water and stirred for 7 minutes. The MnO_2 were electrodeposited on the ITO in three-electrode systems by potentiodynamic method from 6 mM $KMnO_4$ solution in the voltage window of 0.3 V to – 0.5 V at the scan rate of 6 mV s^{-1} for two cycles. After the deposition, the MnO_2 electrode was rinsed in deionized water and dried at 100 °C for 10 minutes. The Cu/MnO_2 composite electrode was obtained by keeping the MnO_2 electrode in 0.1 M $CuSO_4$ solution for 5 electrodeposited cycles in the range of 0.6 V to – 0.6 V at the scan rate of 6 mV s^{-1}. The same processing was employed for ITO to get Cu/ITO electrode. The electrodes were then rinsed in deionized water and dried for 10 minutes.

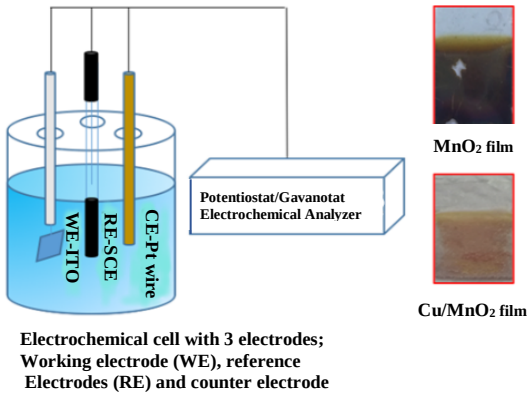

Fig.1 Schematic of the electrodeposition process and the photographs of MnO_2 and Cu/MnO_2 films on ITO substrates

All electrochemical experiments were carried out in standard three-electrode systems under cyclic voltammetry (CV) mode at room temperature using the electrochemical workstation (Corr Test: CS350). The electrodes used are the MnO_2 or Cu or composite Cu/MnO_2 on ITO as working electrode, the saturated calomel electrode (SCE) as reference and Pt as counter electrode. Sodium hydroxide (NaOH) and D-glucose were used for electrolyte solution. Cyclic voltammetry experiments were carried out in quiescent solution. Amperometric measurements, being the measurements of current density resulting from the redox reaction of the electroactive biological element like glucose, were conducted in 50 mM NaOH solution in the absence and presence of glucose at selected potential range.

Results and Discussion

Surface Morphology of MnO_2, Cu and composite Cu/MnO_2 films

The surface morphology of deposited MnO_2, Cu and Cu/MnO_2 thin films were examined by optical microscopy and atomic force microscopy (AFM) as shown in Fig. 2 and 3. The surface of MnO_2 film has good uniformity and coverage seen in the AFM image (Fig. 3 a). However, the surface features are not clearly seen in its optical micrograph (Fig. 2 a). The Cu formed on MnO_2 films have cluster sizes of 1 – 2 μm (Fig. 3 c) while they have larger sizes of around 5 μm on bare ITO substrates (Fig. 3 b). The observed difference in size is attributed to

the different morphology and wettability of different underlying layers. It is also found that the Cu particles are uniformly distributed and have packed morphology on underlying MnO_2 forming a bilayer structure of Cu/MnO_2 composite. The reason is the same as mentioned above.

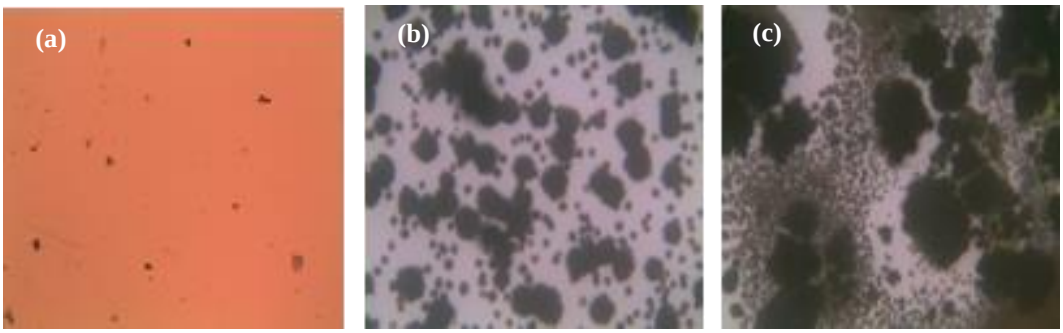

Fig. 2 Optical micrographs of (a) MnO_2 (b) Cu and (c) composite Cu/MnO_2 films on ITO substrates

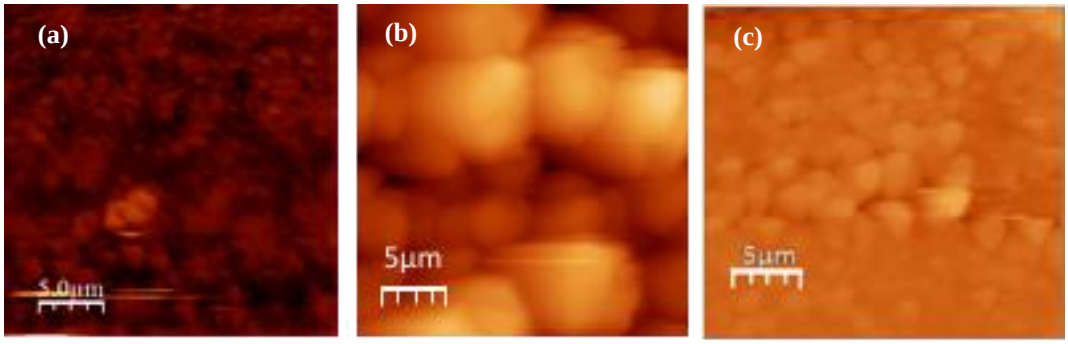

Fig. 3 Atomic force micrographs of (a) MnO_2, (b) Cu and (c) composite Cu/MnO_2 films on ITO substrates

MnO_2, Cu and composite Cu/MnO_2 electrodes for glucose sensing

We examined if the deposited MnO_2, Cu and Cu/MnO_2 film electrodes exhibit a glucose sensing characteristic by acquiring their cyclic voltammograms (CV) in 50 mM NaOH solutions in the absence and presence of 1 mM glucose. Figure 4(a) depicts the CV of MnO_2 electrode which shows no pronounced catalytic effect on the oxidation of glucose. In Fig 4 (b – c), it is obvious that within the operational voltage range of 0.4 – 0.7 V, Cu and Cu/MnO_2 electrodes show corresponding oxidation peaks with current density of 0.7 mA and 1.1 mA respectively. It is obvious that the composition of Cu and MnO_2 shows higher catalytic ability for glucose oxidation than pure Cu indicating that MnO_2 and Cu can cause a synergistic effect for glucose oxidation on the electrode surface. The carriers mechanism for glucose oxidation can be represented by equation (1). The Cu is a transition element having outermost electrons in d-shell which are loosely bound and the Cu/MnO_2 composite has higher reactive surface area so that they can contribute to higher catalytic capability.

$$\begin{aligned} Cu + 2OH^- &\rightarrow Cu(OH)_2 + 2\bar{e} \\ Cu(OH)_2 &\rightarrow CuO + H_2O \\ CuO + OH^- &\rightarrow CuOOH + \bar{e} \end{aligned} \quad (1)$$

Moreover, the fact that Cu/MnO_2 composite electrode has higher sensitivity towards glucose than other MnO_2 and Cu electrodes can be supported by calculating the electroactive surface area using Randles-Seveik relation (equation 2) for a one electron reaction which could be applied at a low scan rate [20].

$$I_p = 2.69 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2} \quad (2)$$

where I_p is the peak current in A, n is the number of electron transfer, A is the electrode area in cm^2,

c is the concentration in mol cm^{-3}, D is the diffusion coefficient in cm^2 s^{-1} and v is the scan rate in V s^{-1}. The D of glucose is 6.7×10^{-6} cm^2 s^{-1} in water. The values of I_p for each electrode are measured in 1 mM glucose at the scan rate of 10 mV s^{-1}. The calculated electroactive surface areas are 0.002, 0.185 and 0.277 cm^2 for MnO_2, Cu and Cu/MnO_2 electrode respectively. A significantly larger electroactive surface area of Cu/MnO_2 electrode would increase its electrocatalytic effect in glucose solution since larger electroactive surface area can promote the transfer of electrons resulting in an increase in oxidation current. In Fig. 4 d, the CV's of MnO_2, Cu and Cu/MnO_2 in glucose solution are selectively plotted so as to clearly visualize that the oxidation current for Cu/MnO_2 is higher as compared to those for other two electrodes MnO_2 and Cu. Higher oxidation current is also attributed to a larger surface to volume ratio for sensing reaction of Cu/MnO_2 which is facilitated by the smaller size of Cu on underlying MnO_2 (Cu size on bare ITO is larger) (see the AFM micrographs in Fig. 3 b and c).

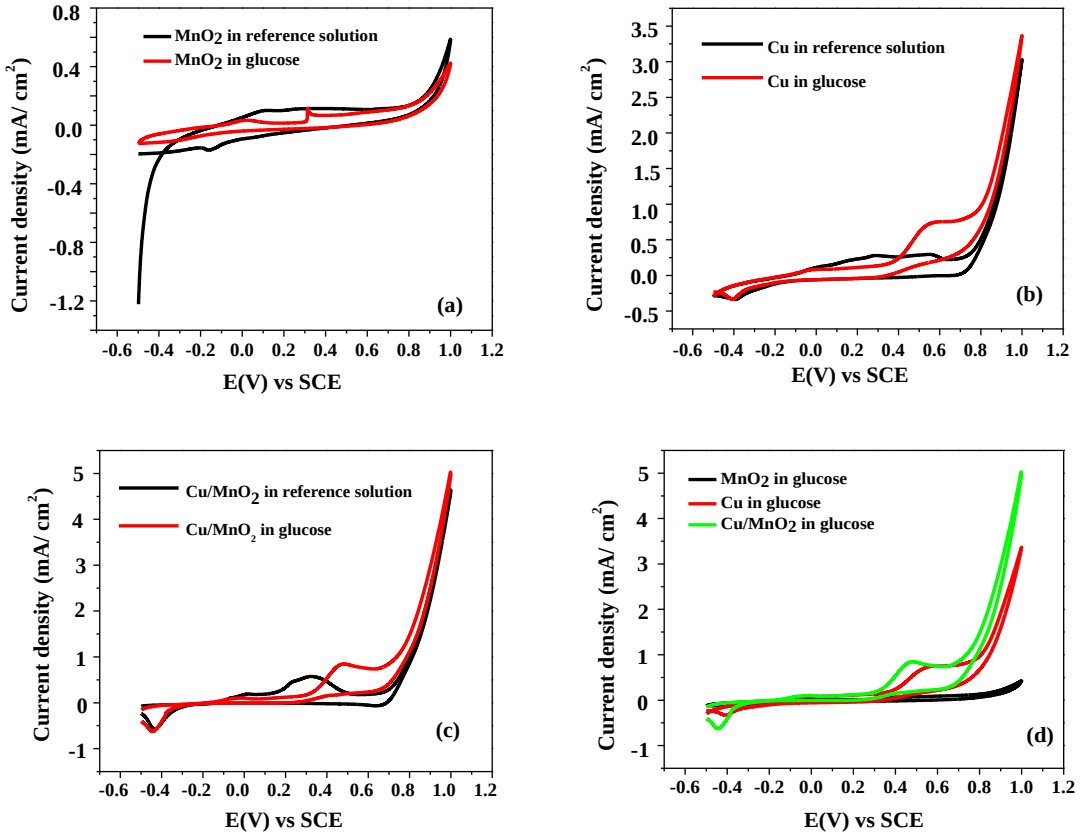

Fig. 4 The cyclic voltammograms (CV) of (a) MnO_2, (b) Cu and (c) Cu/MnO_2 electrodes in the presence and absence of 1 mM glucose in electrolyte (d) CV of MnO_2, Cu and Cu/MnO_2 in 1 mM glucose. The reference is 50 mM NaOH solution and the scan rate is 10 mV s^{-1}.

Next, we studied the dependence of the electrocatalytic performance of composite Cu/MnO_2 electrode on the concentration of glucose and scan rate. Fig. 5 (a) shows the CV's of Cu/MnO_2 electrode in the NaOH solution with various glucose concentrations (0, 0.25, 0.5, 0.75, 1 and 1.25 mM). The plot of peak current density against the glucose concentration is shown in Fig. 5 (b) where the data for 1.25 mM is not shown here since it is deviated from linear trend. The oxidation currents linearly increased with the glucose concentration indicates that Cu/MnO_2 composite electrode has higher catalytic capability for glucose oxidation in the linear range of 0.25 – 1 mM. From the linear correlation plot (Fig. 5 b), the correlation coefficient (R), sensitivity (S) and lower detection limit of Cu/MnO_2 are found to be 0.98, 0.67 mA mM^{-1}

and 0.25 mM respectively. The correlation coefficient was calculated according to equation (3):

$$R = \frac{1}{n-1}\sum_i \left(\frac{x_i - \bar{x}}{s_x}\right)\left(\frac{y_i - \bar{y}}{s_y}\right) \quad (3)$$

where R is the correlation coefficient, x_i and y_i are two variables (former one: concentration of glucose and latter one: measured current density), $\bar{x}$ and $\bar{y}$ are the mean value of the two variables, and S_x and S_y are the standard deviation of the two variables. The sensitivity (S) was acquired from the slope of the linear region in Fig. 5 b.

For the Cu/MnO_2 electrode in 1 mM glucose solution, the CV's were acquired at three different scan rates (10, 50 and 100 mV s^{-1}) as depicted in Fig. 6 a. The scan rate study enables us to understand the reaction mechanism from the relationship between peak current and scan rate. The oxidation reaction of glucose is controlled by the diffusion of gluconolactone on the surface of working electrode. If the electron transfers at working electrode surface is fast, then the current is limited by the diffusion of the species to the electrode surface. A linear dependence of peak current on the square root of the scan rate (Fig. 6 b) is the characteristic of diffusion-controlled process.

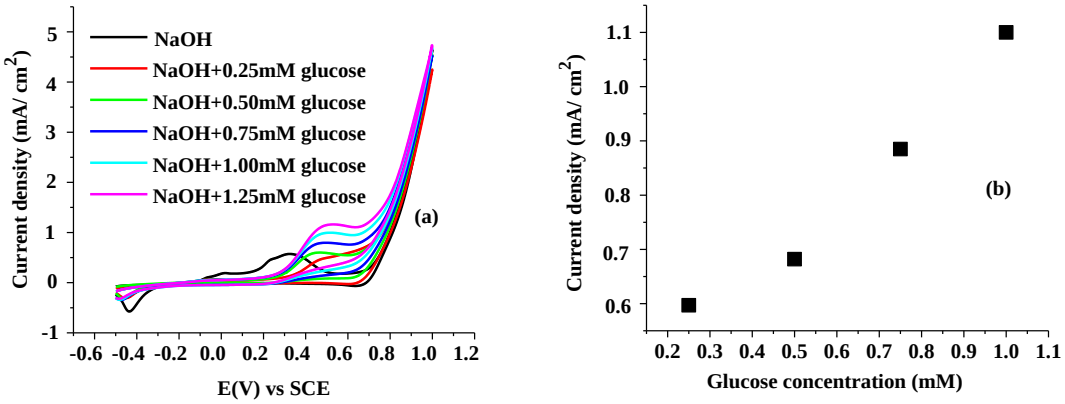

Fig. 5 (a) The cyclic voltammograms (CV) of Cu/MnO_2 in NaOH solution without and with increasing glucose concentration (0.25 – 1.25 mM) at scan rate of 10 mV s^{-1} and (b) Plot of peak current density versus glucose concentration for Cu/MnO_2 electrodes.

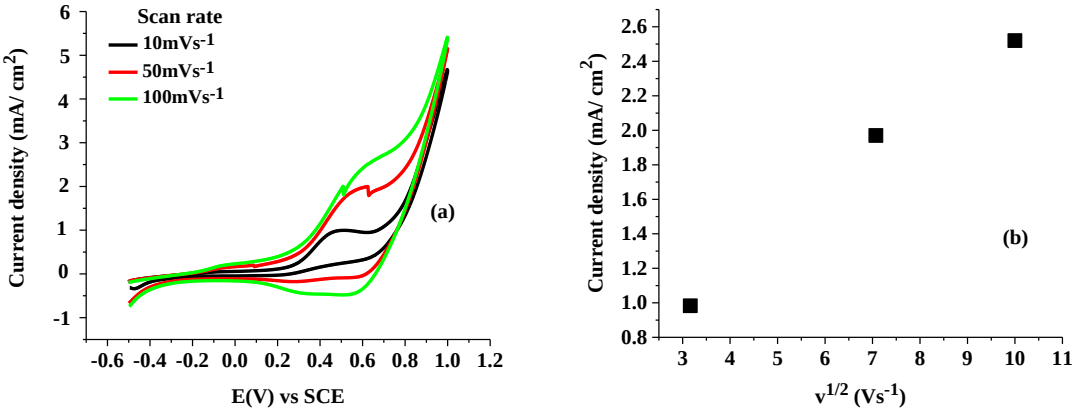

Fig. 6 (a) Cyclic voltammograms (CV) of Cu/MnO_2 electrode in 1 mM glucose solution at different scan rates (10, 50 and 100 mV s^{-1}) and (b) Plot of peak current density versus $v^{1/2}$ for Cu/MnO_2 electrodes.

Conclusion

The MnO_2, Cu, and Cu/MnO_2 composite films were electrodeposited on ITO coated substrates under potentiodynamic mode. Atomic force microscopy study indicated that Cu clusters evenly cover the underlying MnO_2 realizing a bi-layer morphology. The electrochemical cyclic voltammetry characterization showed that the composite Cu/MnO_2 electrode outperformed the pristine MnO_2 and Cu electrode in glucose sensing. It is attributed to a better catalytic ability of Cu/MnO_2 electrode towards glucose oxidation through synergistic effect. A linear correlation of the oxidation current densities of Cu/MnO_2 against glucose concentration suggested that the electrode sensitivity is 0.67 mA mM^{-1} and lowest detection limit is 0.25 mM. To sum up, the Cu/MnO_2 composites are promising for glucose sensor application and the present study suggests a way to achieve a better sensing characteristic through further optimization of the morphology and size of sensing materials, thereby improving the electron transfer between the sensing reaction and electrode

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