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Enzymeless glucose biosensor using CuO nanoparticles on amine-functionalized carbon nanotubes

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Abstract:

CuO nanoparticles on amine-functionalized multi wall carbon nanotubes (CuO/A-MWCNTs) were easily prepared by a fixture-reduction method and used for sensing glucose without GOx. The morphology and structure of the CuO/A-MWCNTs were characterized by FESEM, XRD, and ICP for its Cu content. Cyclic voltammetry and chronoamperometery were used to show the electrochemical and electrocatalytic activity of the nanocomposite towards glucose detection. Comparison between bare GCE, CuO/GCE, A-MWCNTs/GCE and CuO/A-MWCNTs/GCE, indicates that CuO/A-MWCNTs modified electrode have the greatest ability to detect glucose with a low detection limit of 1.0 μM and linear range from 100 μM to 1.5 mM. The modified electrode with a simple synthesis procedure can be used for a highly stable enzymeless glucose sensor.

Key words: Enzymeless glucose biosensor, carbon nanotubes , CuO nanoparticles, amine-functionalized MWCNT.

Introduction

In vivo measurement of glucose concentration in human blood for about 5% of the World's population who suffer from diabetes is very crucial. Enzymatic, (using glucose oxidase (GOx)) and nonenzymatic sensors are two types of amperometric method for glucose sensing. Enzymatic sensors have great sensitivity and selectivity [1] but enzymes due to their natures, do not have stability and also GOx activity is easily affected by pH, temperature, humidity and toxic chemicals [2]. Therefore, very much efforts have been put to develop enzymeless sensors to achieve good sensitivity, selectivity, low detection limit and the most important, high stability.

Functionalized CNTs are extensively used for modification of electrochemical biosensor electrodes. In comparison with other functionalization methods, plasma showed to be a better, faster, cleaner and the most important, MWCNTs are less damaged and not being shortened [3].

Metal nanoparticles (NPs) recently have been used for different applications in many disciplines such as chemistry, physics, biology and medicine due to their special catalytic properties [4]. Many NPs such as Au , Pt [5], Cu [6] and Ni [7] have been used to enhance electrochemical activities in biosensors.

In the current study, amine-functionalized MWCNTs with improved interaction between CNTs and NPs were used to prepare CuO/A-MWCNTs by a simple method. The prepared CuO/A-MWCNTs showed very good electrocatalytic activity and is applied as an enzymeless glucose biosensor.

Experimental

Multi wall carbon nanotubes (MWCNTs) (10-20 nm diameter and 10-30 μm length with >95% purity) were purchased from Neutrino Co. KH_2PO_4 , K_2HPO_4 , $Cu(Ac)_2$ and D(+)–Glucose (97%) were purchased from Merck. Nafion (5 wt.%) was purchased from Sigma-Aldrich. All other reagents were of analytical grade. Deionized water was used for preparation of all aqueous solutions. MWCNTs were heated in the dielectric barrier discharge (DBD) plasma reactor under He atmosphere (to degas CNT) up to 100°C to achieve activated CNTs that contains active sites on their walls and ends and they will be ready to adsorb ammonia. Diluted ammonia with He were passed over MWCNTs being kept at about 200°C for 1 h and then cooled and only He was passed for few minutes to remove any physical adsorption of ammonia on the surface of CNTs. With this simple procedure, functionalized MWCNTs were obtained and A-MWCNTs were ready to

use [3]. A-MWCNTs were then dispersed in the cupric acid solution and CuO nanoparticles were formed on the side of the CNTs by hydrothermal process[8]. 10 µlit of CuO/A-MWCNTs in a solution of nafion and deionized water was dropped on the surface of GCE (glassy carbon electrode (3mm in diameter)) and dried.

Results and discussion

Figure 1 shows the XRD pattern of CuO/A-MWCNTs. The XRD results clearly indicate the presence of CuO.

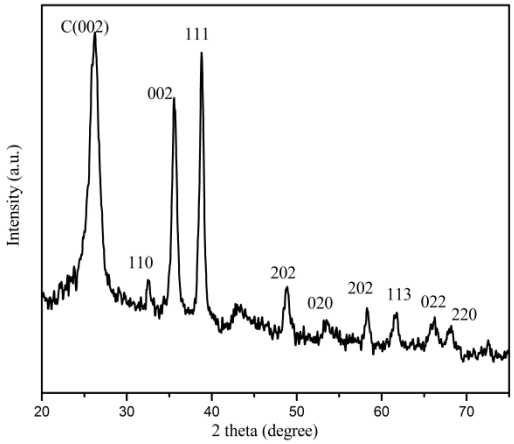

Fig. 1. XRD pattern of CuO/A-MWCNTs.

Figure 2 presents the CVs of different modified GCEs electrodes, which has been modified with A-MWCNTs, CuO, CuO/A-MWCNTs. As it is clear, the combination of MWCNTs and Cu in comparison with single CuO or A-MWCNTs reveals a very high current that shows the very good electrochemical activity of this nanocomposite (CuO were prepared with the same procedure as CuO/A-MWCNTs but without A-MWCNTs).

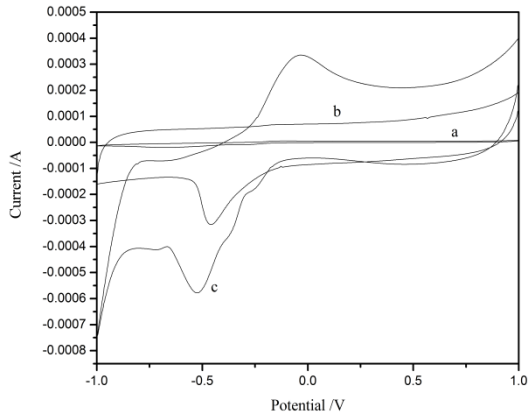

Fig. 2. Cyclic voltammetry of different modified electrodes at 30 mV/s in 0.05 M PBS. a:CuO , b:A-MWCNTs , c:CuO/A-MWCNTs.

ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) analysis showed 34% Cu in the composite. We used a nominal ratio of 60:40 for A-MWCNT:Cu for synthesis of the composite. However, we have lost a little of Cu and most of the Cu precursor was deposited on A-MWCNTs. Figure 3 shows cyclic voltammetry of this modified electrode in 0.05 M PBS in the scanning potential from -1 to 1 with 30 mV/s as scanning rate. In this Figure 2 sharp peaks in forward and reverse scans are shown. The anodic peak goes up and cathodic one goes down by increasing the glucose concentrations which indicate the detection of glucose.

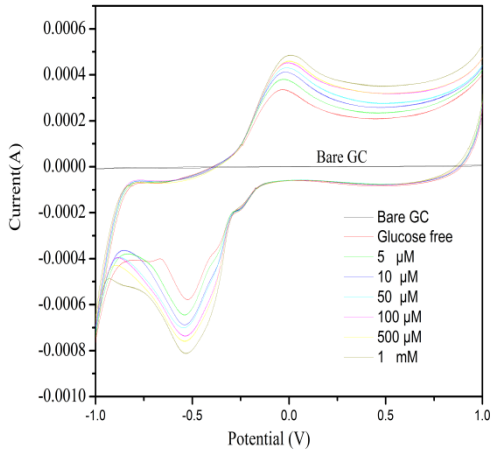

Fig. 3. Cyclic Voltammetry of CuO/A-MWCNTs in PBS (0.05M) at 30 mV/s in the absence and presence of glucose (in different glucose concentration).

The current-concentration measurement is shown in Figure 4. By increasing the glucose concentration a linear range between 100 µM to 1.5 mM with R^2= 0.993 illustrates a good catalytic activity for detection of glucose.

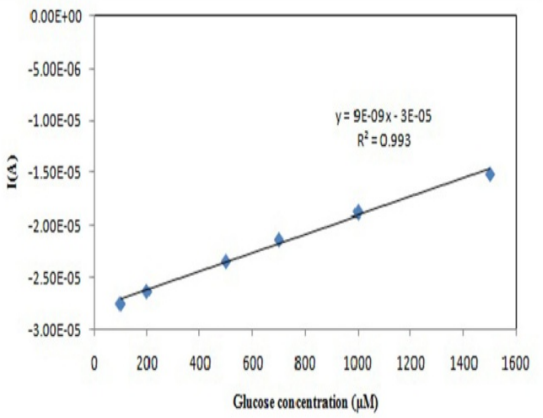

Fig. 4. Amperometric linear response for CuO/A-MWCNTs modified electrode at different glucose concentration.

Thus, CuO/A-MWCNTs modified electrode shows the greatest ability to detect glucose with a low detection limit of 1.0 μM in comparison to other electrodes reported in the literature.

Conclusion:
We have successfully fabricated an electrode modified with CuO nanoparticles on amine-functionalized carbon nanotubes (A-MWCNTs) for detection of glucose without using GOx. The CuO/A-MWCNTs electrode exhibited a good electrocatalytic activity toward glucose oxidation with a low detection limit of 1 μM and linear range of 100 μM to 1.5 mM. Therefore the CuO/A-MWCNTs modified electrode can be used for detection of low glucose concentrations.

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