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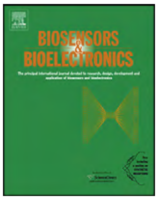

Short communication

An amperometric non-enzymatic glucose sensor by electrodepositing copper nanocubes onto vertically well-aligned multi-walled carbon nanotube arrays

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ABSTRACT

A non-enzymatic glucose (Glc) sensor was developed by potentiostatically electrodepositing metallic Cu nanocubes from a precursor solution onto vertically well-aligned multi-walled carbon nanotube arrays (MWCNTs). The electrochemical characteristics of the sensor were studied by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The sensor shows significantly higher electrocatalytic activity to the oxidation of Glc in 0.1 M NaOH alkaline solution after modification of Cu nanocubes than before. The sensor response is rapid (<1 s) and highly sensitive (1096 μA mM^{-1} cm^{-2}) with a wide linear range (up to 7.5 mM) and low detection limit (1.0 μM at signal/noise ratio (S/N) = 3); it also exhibits high stability and specificity to Glc and performs very well in detecting of Glc concentration in human blood serum.

1. Introduction

The pursuit of a rapid, simple, inexpensive, and reliable Glc sensing is on going for various applications including for clinical application of blood Glc sensing, ecological application of industrial waste water treatment and food application of dietary and obesity control. Glc enzyme electrodes based on glucose oxidase (GOx), which oxidizes Glc into gluconic acid in the presence of oxygen by direct electron transfer has been widely investigated (Deng et al., 2008). However, due to the intrinsic properties of enzymes, the catalytic activity of GOx is susceptible to environmental conditions such as temperature, humidity, pH, ionic detergents, and toxic chemicals (Wilson and Turner, 1992). Furthermore, GOx sensors suffer from high cost, poor stability, need for critical operational conditions, oxygen, and complicated immobilization procedures usually associated with adsorption, and cross-linking and entrapment in an electropolymerized and biocompatible matrix (Yang et al., 2006). Therefore, simple enzyme-free Glc sensing is highly desirable. Much work has been done to develop enzyme-free Glc sensors (Kang et al., 2007; Wang et al., 2008a,b; Batchelor-McAuley et al., 2008a; Zhuang et al., 2008). However, most non-enzymatic sensors undergo surface etching during electrochemical processes or surface poisoning by intermediate species and chloride ions (Cl$^-$) (Ye et al., 2004), and thus suffer from low sensitivity, narrow linear range, high cost of rare metal precursors, bad performance in complex matrices and poor specificity to Glc.

Cu is one of the widely investigated metal catalysts and its electrodeposition has been studied on various carbon scaffolds (Ghodbane et al., 2007). The unique structural, physical, and chemical properties of nanoscaled materials are closely related to both their size and shape (Zhang et al., 2008). For example, cubic Pt particles are said to exhibit higher catalytic activity with more effective and active sites, than spherical particles (Yamada, 2009). Thus, controlling the nanomaterial morphology is an effective way to impart certain unique properties to nanostructured materials. Synthesis of various nanostructures has been achieved using different techniques: cubes (Chen et al., 2007; Claussen et al., 2009), flowers (Yu et al., 2008), wires (Zhuang et al., 2008), platelets (Wang et al., 2008a,b), spindles (Zhang et al., 2008), rods (Ren et al., 2009) and prisms (Pal et al., 2009). For example, Zhang et al. (2008) synthesized CuO nanostructures of wires, platelets, and spindles and used them for Glc sensing by simple wet-chemistry and Kang et al. (2007) electrochemically deposited Cu nanoclusters onto a MWCNTs-modified glassy carbon (GC) electrode. However, most fabrications of nanostructures involve complicated multi-steps.

Herein, we describe a simple electrodeposition method to synthesize novel nanocomposites of Cu nanocubes and MWCNTs for Glc sensing, which has not been reported. MWCNTs arrays were grown on Ta substrate by catalytic vapor deposition (Zhang et al., 2002) and Cu nanocubes were electrochemically deposited onto the MWCNTs arrays by a simple cathodic potentiostatic technique. The Cu-modified MWCNTs electrode shows considerably higher

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electrocatalytic activity for Glc than the unmodified MWCNTs. This new nanocomposite material combines the advantages of Cu nanocubes and MWCNTs arrays (Katz and Willner, 2004) and could exhibit a synergistic effect. The Cu-MWCNTs nanocomposite electrode exhibits high sensitivity, stability, and specificity for Glc. Its response is rapid with a wide linear range, a low detection limit and good performance in detecting Glc content in blood serum. These qualities make the Cu-MWCNTs electrode a promising candidate for enzyme-free amperometric Glc sensing.

2. Experimental

2.1. Chemicals and reagents

D(+)-Glucose, L-ascorbic acid (AA), uric acid (UA), dopamine (DA), D-fructose, mannose, and lactose were purchased from Alfa Aesar. All other reagents were of analytical grade and were used as received without further purification. All solutions were freshly prepared with high-quality deionized water (resistivity > 18.4 MΩ cm^{-1}).

2.2. Instruments

XRD profiles of Cu-modified MWCNTs were obtained (XD-3A, Shimadzu) with high-intensity Cu Kα radiation ($\lambda = 1.5406$ nm). Morphologies and nanostructures of vertically-aligned MWCNTs arrays and Cu nanotubes were determined using transmission electron microscopy (TEM) (Hitachi H7650, Tokyo, Japan) and scanning electron microscopy (SEM) (Hitachi S-3700N, Tokyo, Japan) which is equipped with energy dispersive X-ray spectroscopy (EDS) to analyze surface elemental composition. Chemistry analyzer (Synchron CX9, Clinical System, Beckman, USA) was used to determine Glc content in human blood serum (kindly provided by Nanfang Hospital, Guangzhou, China) within 1 h of drawing blood to compare with results from our sensors.

Electrochemical measurements and EIS were performed on a CHI 660C electrochemical analyzer (Shanghai, China) and data were analyzed with CHI software. A conventional three-electrode configuration was used: Ag/AgCl (3 M KCl) reference electrode, Pt wire counter electrode, and a working electrode (unmodified or Cu-modified MWCNTs). All potentials were referenced to the Ag/AgCl (3 M KCl) electrode. EIS was performed with the same three-electrode configuration in an electrolyte solution of 100 mM KCl containing equimolar $[Fe(CN)_6]^{4-/3-}$, in a frequency range from 0.1 Hz to 100 kHz with an ac probe amplitude of 5 mV.

2.3. Preparation of the Cu-MWCNTs nanocomposite electrode

MWCNTs arrays were synthesized employing the catalytic chemical vapor deposition technique on 3 mm × 3 mm Ta foils (Zhang et al., 2002) and were used as unmodified MWCNTs electrode by connecting it to the surface of a GC electrode with a conductive silver paint (Structure Probe Inc., USA). Nail enamel (Maybelline, USA) was used to insulate edges of the electrode for further electrodeposition of Cu nanocubes. The copper nanocubes were electrochemically coated onto the MWCNTs array by potentiostatic deposition. A precursor solution of 10 mM $CuCl_2$ and 100 mM KCl was used as the copper source. A constant potential of −0.40 V was applied to the MWCNTs electrode for 120 s, which was previously determined to be the optimal duration to achieve the best electrocatalytic performance. All experiments were performed at room temperature (25 ± 1 °C). Solutions were pre-purged with N_2 for at least 15 min to remove O_2, while a continuous flow of N_2 was maintained during experiments. The configuration of the Cu-MWCNTs electrode is shown in Cherevko and Chung, 2010; Li et al., 2009; Scheme S1.

3. Results and discussion

3.1. Structural characterization

A typical XRD profile of as-prepared Cu-MWCNTs is shown in Fig. 1A. The peaks labeled with * indicate reflections from Ta substrate (JCPDS 04-788) and those with # at 2θ of around 43° and 95° were very close to the profiles of metallic Cu (JCPDS 04-0836). No additional peaks of Cu or of other impurities or oxidation of Cu_2O/CuO were seen. The obvious peak observed at $2\theta = 22.4°$ was attributed to graphite carbon C(0 0 2) (JCPDS 75-1261). Elemental compositions of Cu-MWCNTs were analyzed by EDS (Fig. 1B). Ta, O and Co elements were observed for unmodified MWCNTs arrays. The peak of Ta was from the substrate and the small amount of Co originated from the catalyst used during MWCNTs synthesis (Chen et al., 2008). In comparison, Cu was only observed in the spectrum of Cu-MWCNTs, suggesting Cu was successfully electrodeposited onto the MWCNTs.

Fig. 1C shows the TEM images of MWCNTs and Cu-MWCNTs. Before modification (Fig. 1C, inset), the nanotubes were smooth, with the tubular diameter of 110.8 ± 5.5 nm (six measurements), consistent with the range of 80–120 nm reported in the literature (Ye et al., 2003). After electrodeposition, the tip and sidewalls of MWCNTs were embellished with solid Cu nanocubes, giving them a high aspect ratio and large surface area. The morphology of the Cu deposits is clearly cubical with fairly uniform edge dimensions from 20 nm to 70 nm. Larger and more numerous nanocubes are present at the MWCNTs tip than at other locations, owing to the high static attraction at the tip during electrodeposition.

The morphology and structure of MWCNTs and Cu-MWCNTs were further investigated with SEM. The nanotubes were found to be vertically well-aligned with part of the nanotubes peeled off for easy observation (Fig. 1D). The surface of the unmodified MWCNTs is fairly clean and smooth (Fig. 1D, inset), whereas that of Cu-MWCNTs becomes rough with cubical Cu particles attached to the sidewalls and tips (Fig. 1E). The majority of Cu particles have a uniform cubic structure. Fig. 1E(inset) confirms the attachment of cubical Cu nanoparticles on to MWCNTs.

Though the detailed mechanism of electrochemically forming the Cu nanocubes is unclear, anion species present in the solution and the MWCNTs arrays are believed to play an important role. Anions are generally absorbed onto a crystal surface and can affect the growth rates between facets of nanoparticles (Yamada, 2009), and the additive effect of a salt can achieve cubic selectivity of up to 84% (Yamada et al., 2005). In our system, Cl^- present in the Cu plating solution can form aqueous Cu(I)–Cl^- complexes and induce strong Cl^-–Cu surface adsorption interactions to affect the kinetics of Cu electrodeposition (Chassaing and Wiart, 1984). During nucleation under a low cathodic overpotential, Cu surface is covered by chloride-containing anion species (Magnusen, 2002) and can therefore hinder the electrodeposition. The anisotropy of Cu electrodeposits can be ascribed to the Cu(I)–Cl^- complexes interacting with different copper surface lattice sites (Yamada, 2009) and can determine the rate and morphology (Wu and Barkey., 2000). Furthermore, the interaction of Cl^- and Cu nuclei surfaces might also be involved, which could reduce growth rates and generate a highly anisotropic growth for Cu nanocubes, similar to the 'poisoning' mechanisms for the anisotropic growth of other materials (Almeida and Alcacer, 1983).

In the absence of organic additives, the cathodic electrodeposition of Cu nanocubes can be described as:

$$Cu^{2+} + 2Cl^- + e^- \rightleftharpoons CuCl_2{}^-$$

$$CuCl_2{}^- + e^- \rightleftharpoons Cu + 2Cl^-$$