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In situ attachment of cupric oxide nanoparticles to mesoporous carbons for sensitive amperometric non-enzymatic sensing of glucose

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ABSTRACT

A convenient method was developed to directly attaching cupric oxide nanoparticles (CuONPs) on mesoporous carbons (MCs) for sensitive amperometric non-enzymatic sensing of glucose. The CuONPs–MCs nanocomposite was characterized with transmission electron microscopy and X-ray diffraction. Based on the advantageous functions of CuONPs and MCs, the functional nanocomposite modified glassy carbon electrode showed high electrocatalytic activity toward the oxidation of glucose. Due to the electrocatalytic activity to glucose, a non-enzymatic glucose sensor was constructed based on the CuONPs–MCs nanocomposite. Under optimal experimental conditions, the designed sensor exhibited a wide linear response to glucose ranging from 4×10^{-7} to 7.3×10^{-3} M with a high sensitivity of 1154.1 $\mu A\,mM^{-1}\,cm^{-2}$ and a low detection limit down to 0.1 μM at the signal to noise ratio of 3. This sensor showed good accuracy, acceptable precision and reproducibility. The assay results of glucose in human blood serums with the proposed method were in a good agreement with the reference values. The functionalization of MCs with CuONPs provided good biocompatible platform for sensing and catalysis.

1. Introduction

Diabetes mellitus is a worldwide public health problem that seriously affects the normal life of hundreds of million people [1]. Blood glucose level is a basic issue in the diagnosis and treatment of diabetes. Therefore, the monitoring of blood glucose level is of great importance in the diagnosis and management of diabetes. Electrochemical sensors have been considered as the best candidates for the in situ detection of glucose because of the simplicity, fast response and easy miniaturizing. Due to the good selectivity and high sensitivity, electrochemical glucose biosensors based on glucose oxidase have been widely investigated [2–4]. However, there are some disadvantages with these enzymatic biosensors, such as poor stability, reproducibility [5] and high cost of enzymes. Thus, it is much imperative to develop non-enzymatic glucose sensors based on specific materials.

A variety of materials have been explored to construct non-enzymatic glucose sensors including metals (e.g., Au [6,7], Pt [8–10], Pd [11,12], Ni [13,14], Cu [15,16]), alloys (e.g., CuNi [17], PdNi [18], PbPt [19], NiTi [20], PdPt [21], PtRu [22]) and metal oxides (e.g., CuO [23–25], Co_3O_4 [26], MnO_2 [27], NiO [28]). Among these materials, cupric oxides nanoparticles (CuONPs), as a p-type semiconductor, has been study in the electrochemical application such as batteries [29] and sensors [30]. Due to the electrocatalytic effect mediated by Cu(III)/Cu(II) redox couple [31,32], CuONPs showed good electrocatalytic performance in the direct electrooxidation of glucose. In order to further improve its conductivity for preparation of glucose sensors, a CuONPs–carbon nanotubes (CuONPs–CNTs) composite had been synthesized [33,34]. The presence of CNTs could facilitate the charge transfer and improve the sensitivity of resulting glucose sensors. This work prepared a novel CuONPs-nanocomposite, CuONPs–mesoporous carbons (CuONPs–MCs) composite.

Mesoporous carbons (MCs), as a 3-D nanostructured porous materials, has recently emerged as an intriguing material for potential applications in catalysis [35], batteries [36,37] and sensors [21,38]. Compared with CNT, MCs had better electrochemical and electrocatalytic properties due to the high density of edge plane-like defective sites and a large surface area [39]. Extensive favorable sites on MCs for electron transfer to compounds made MCs a novel material for the application in electronic devices [38]. Moreover the MCs could serve as the conductive carbon matrix and help to homogeneously separate PtNPs [40], AuNPs [41] and MnO_2 [42]. This work prepared sensitive non-enzymatic glucose sensors based on CuONPs–MCs composite.

The CuONPs–MCs composite was conveniently prepared by one green chemical step to directly attach CuONPs on MCs without needing pre-surface modification. The morphology and composition were investigated by transmission electron microscopy (TEM) and X-ray diffraction, respectively. CuONPs–MCs composite

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modified glassy carbon electrode (CuONPs–MCs/GCE) showed high electrocatalytic activity toward the oxidation of glucose. Due to the electrocatalytic activity to glucose at the CuONPs–MCs/GCE, a non-enzymatic glucose sensor was constructed. The designed sensor showed good performance with a wide linear range, a low detection limit, acceptable precision, reproducibility and stability for the determination of glucose. It was successfully applied in the detection of glucose in human blood serum. CuONPs–MCs/GCE nanocomposite provided a biocompatible platform for sensing and catalysis.

2. Experimental

2.1. Reagents

Triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, M_w = 12,600) and polyethylene glycol (PEG, M_w = 200) were purchased from Sigma–Aldrich (USA). D-Glucose was purchased from Shanghai Run Jie Chemical Reagent Co. Ltd. (China). Tetraethyl orthosilicate (TEOS), aqueous ammonia (28 wt.%), formalin solution (37 wt.%), phenol, ethanol, copper nitrate trihydrate, potassium chloride and uric acid (UA) were obtained from Sinopharm Chemical Reagent Co. Ltd (China), and N,N-dimethyl formamide (DMAC) from Shanghai Ling Feng Chemical Reagent Co. Ltd. (China). NaOH and scorbic acid (AA) were purchased from Shanghai No. 4 Reagent & H.v Chemical Co. Ltd. (China) and dopamine (DA) from New Jersey, USA. All other reagents were of analytical grade and used without further purification. Deionized water was used for the preparation of all solutions.

2.2. Apparatus

Transmission electron microscopic (TEM) images were gained on a JEM-2100 TEM (JEOL, Japan). X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 diffractometer with an area detector operating under a voltage of 40 kV and a current of 100 mA using Cu Kα radiation (λ = 0.15406 nm). Brunauer–Emmett–Teller (BET) specific surface area of MCs was determined from N_2 gas adsorption–desorption measurements by ASAP 2010C surface area and porosimetry analyzer (Micromeritics Instruments Inc., USA). By using the Barret–Joyner–Halenda (BJH) model, the pore size distribution were derived from the desorption branches of isotherms. Electrochemical experiments were performed on a CHI 660D electrochemical analyzer (Co. CHI, USA) with a conventional three-electrode system with a modified GCE as working, a platinum wire as auxiliary and a saturated calomel electrode as reference electrode, respectively. All experiments were carried out at room temperature.

2.3. Synthesis of MCs

MCs were prepared by a facile dual-templating approach according to the previous literature [43] with slight modification. 5.0 g carbon source of soluble phenolic resin prepared by the reported method [44] was added into 1.27 g triblock copolymer F127 as a soft template in ethanol solution, and the above solution mixed with 1 g monodispersed silica colloidal microspheres used as a hard template. The mixture was evaporated at 25 °C for 48 h, dried at 100 °C under a vacuum tank for another 24 h and carbonized in tube furnace in N_2 at 700 °C for 5 h at a heating rate of 1 °C min^{-1}. The black powder was washing with 15% aqueous HF solution and activated with 1 M NaOH solution at 60 °C for 3 h to remove the SiO_2 template, followed by washing with deionized water and drying at 100 °C in a vacuum for 24 h to obtain MCs.

2.4. Preparation of CuONPs–MCs nanocomposite

CuONPs–MCs nanocomposite was prepared by a simple precipitation procedure. 0.334 g $Cu(NO_3)_2{\cdot}3H_2O$ and 0.010 g MCs were added in 100 mL DMAC, and the suspension solution was sonicated and stirred for 20 min for six times. After stirring overnight, 48 mL of DMAC/water (5:1, v/v) solution containing 2.8 mM NaOH was rapidly added into the mixture at 100 °C, followed by vigorously stirring for 10 min. The resulting solution was heated to 110 °C for 30 min. After being cooled at room temperature, this dispersion was filtered, washed with ethanol and deionized water and dried to get CuONPs–MCs nanocomposite. CuONPs were prepared with the same method in absence of MCs [45].

2.5. Preparation of modified electrodes

The glassy carbon electrode (GCE, 3 mm diameter) was polished with 0.05-μm alumina slurry (Beuhler), followed by rinsing thoroughly with doubly distilled water. After successive sonication in 1:1 nitric acid, ethanol and deionized water, the electrode was rinsed with deionized water and allowed to dry at room temperature. CuONPs–MCs modified GCE (CuONPs–MCs/GCE) was prepared by dropping 4 μL of different concentrations of CuONPs–MCs suspension on the pretreated GCE and drying at room temperature. As control, CuONPs modified GCE (CuONPs/GCE) and MCs modified GCE (MCs/GCE) were prepared with the same procedure.

3. Results and discussion

3.1. Characterization of CuONPs–MCs nanocomposites

Fig. 1 displays the typical TEM images of MCs and CuONPs–MCs. MCs showed a hierarchical mesoporous structure (Fig. 1A). The BET specific surface area of MCs was 200 m^2/g and the pore size calculated from BJH model ranged 5 to 70 nm, which may be favorable to the attachments of nanoparticles and protein molecules. As shown in Fig. 1B, CuO nanoparticles were homogeneously dispersed in the pores or on the walls of the MC without obvious aggregation. As control, the CuONPs prepared with the same method in absence of MCs aggregated together (Fig. 1C). This result indicates that during synthesis MCs acts as carbon matrix, thereby homogeneously separating CuONPs.

Fig. 1D shows the XRD patterns of CuONPs, MCs and CuONPs–MCs nanocomposites. The broad diffraction peak with 2θ value of around 23.3° was attributed to the plane of (0 0 2) of graphite of MCs. There were mainly four peaks with 2θ values of 35.56°, 38.75°, 48.70° and 61.55° corresponding to (−1 1 1), (1 1 1), (−2 0 2) and (−1 1 3) crystal planes of pure CuONPs (JCPDS 48-1548) and the CuONPs on CuONPs–MCs nanocomposite, indicating that the CuONPs successfully loaded on the surface of MCs. No reflections for $Cu(OH)_2$ was observed, which suggested the $Cu(OH)_2$ was completely converted into CuONPs during the chemical deposition.

3.2. Electrochemical performance of glucose at CuONPs–MCs/GCE

The electrocatalytic activity of the CuONPs–MCs/GCE toward oxidation of glucose was investigated by cyclic voltammetry (Fig. 2). In 0.05 M NaOH solution, GCE (curve a) and MCs/GCE (curve b) did not show any redox peak in the working potential range, while CuONPs/GCE (curve c) and CuONPs–MCs/GCE (curve d) displayed a single reduction peak at 0.60 V and 0.56 V, respectively, assigning to a Cu(III)/Cu(II) redox couple [28–30]. However, the corresponding oxidation peak of Cu(II)/Cu(III) within +0.40 to +0.80 V was not clearly observed at the CuONPs–MC/GCE and CuONPs/GCE, which could be overlaid by the oxidation peak of water-splitting