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Facile synthesis of copper oxide microflowers for nonenzymatic glucose sensor applications

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ABSTRACT

In this manuscript, an attempt has been made to synthesize well-crystallized flower-shaped copper oxide hierarchical structures by simple solution process for fabrication of nonenzymatic glucose sensor under alkaline conditions. Scanning and Transmission electron micrographs clearly illustrate that CuO structures are flower-like shape while X-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) analyses indicate the formation of pure CuO monoclinic phase. Modified electrode with CuO microflowers shows a wide linear response towards glucose in the concentration range of 10–120 μM with a detection limit of 6.48 μM (S/N = 3). Such results have revealed that CuO microflowers show excellent electrocatalytic activity and efficient electron transport property; hence it may be a promising candidate for the nonenzymatic glucose sensor applications.

1. Introduction

Accurate glucose detection is the most important analytical applications for scientists in biotechnology, food industry, etc., which is important for clinical assessments in the diabetic control center. In general, the blood glucose range is 3.6 − 7.5 and 1.1 − 20.8 mM for healthy people and diabetic patients, respectively. Therefore, it is appropriate to examine and develop nonenzymatic sensors with high sensitivity and low detection limit to achieve convincing clinical measurements. Standard measurements of glucose level in blood are required to determine whether the treatments are working efficiently for diabetic patients. Numerous drawbacks emerged with high-cost enzyme-modified electrodes towards biosensors since it is unstable to a complete long-term stability based on the environmental condition [1]. To overcome such problems considerable concentration had been compensated for developing non-enzymatic electrodes. Thus, there is an increasing necessitate for especially nonenzymatic amperometric biosensor [2] to generate electrochemical glucose sensors with elevated sensitivity, high reliability, good recyclability, short response times and inexpensive.

Currently, researchers put trying to improve the sensitive non-enzymatic glucose sensor using diverse materials, such as metals (platinum, gold, copper), alloys (including Pt, Pb, Au, Pd, Ir and Ru) and metal oxide (IrO_2, MnO_2 and CuO) [3–12]. Highly active surface area of the modified electrode substrates plays a key role in the electrooxidation of glucose. The disadvantage of metal modified electrodes for glucose sensors is their lack of stability due to ready oxidization in air and solution then poisoning by adsorbed intermediates [13]. To concentrate on this problem, several efforts have been made to develop glucose sensors with some nanostructured electrodes that have been reported to develop innovative nonenzymatic glucose sensors, i.e., majorly metal oxide nanostructures as simulated intermediaries between the electrodes and the analytes [14–16].

Metal oxide nanostructures have attracted remarkable attention due to their unique assets for several appliances [17]. Sensitivity and catalytic properties depend on size and shape of nanostructured metal oxides [18,19]. Among various metal oxides, the p-type CuO is a distinctive semiconductor monoxide with a narrow band gap (1.2 eV) has attracted due to its nontoxic, high stability and inexpensive of the material [20]. The synthesis of the CuO nanostructures is very important due to its both crucial investigations and realistic applications such as batteries, heterogeneous catalysts, sensors, supercapacitors and field emission emitters [21–24]. Recently scientists have been many efforts directed towards the synthesis of CuO micro-/nanostructures such as nanoparticles, nanoplates, nanoflowers, nanorods/wires, nanoribbons, micro-dandelions, hollow spheres, spindles, nanofilms, and hierarchical nanostructures and only a few of them were examined for sensing applications [25–36]. While CuO crystals with the various

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morphologies described above have been successfully synthesized, most of the present architectural structures are on larger scales, which confine their potential applications. Previous attempts are limited by complex fabrication processes and the fabricated sensors exhibit a poor linear detection range. Properties of materials at nanoscale strongly depend on their shape and dimensions. It would be interesting to seek simpler processes for the synthesis of different CuO nanostructures with superior catalytic properties for fast, sensitive, and stable detection of glucose. In order to further improve the surface area, the synthesis a new category of CuO micro flowers with a much smaller size or made from higher activity building blocks is imperative. For example, Zhang et al. [37] reported cuprous oxide microcubes for nonenzymatic amperometric hydrogen peroxide and glucose sensing. Sun et al. [38] establish a facile water-assisted synthesis of cupric oxide nano urchins for nonenzymatic glucose biosensor. Wang et al. using Cu-CuO nanowire composites reported enzyme-free amperometric sensing of glucose [39].

In this manuscript, a simplistic approach was followed for developing an enzymeless glucose sensor based on CuO microflowers grown by simple solution process and utilized as an efficient performance nonenzymatic glucose sensing without immobilization of expensive enzymes. The nonenzymatic glucose sensor based on these CuO MFs show high sensitivities with low detection limit. Upon comparison with the literature, the observed detection of glucose is promising at low oxidation potential since the regular interfering molecules would not be oxidized at low oxidation potential. Finally to exhibit the electrocatalytic ability of CuO MFs modified electrode the detection of glucose in the real serum sample was effectively demonstrated.

2. Experimental details

2.1. Materials

Copper (II) nitrate trihydrate [($Cu(NO_3)_2{\cdot}3H_2O$], hexamethylenetetramine [HMTA, $C_6H_{12}O_4$], Nafion (5% wt in alcohol), D-glucose, ascorbic acid, dopamine and uric acid were purchased from Sigma Aldrich. All other chemicals from commercial sources were of analytical grade and aqueous solutions were prepared with double distilled water (DD). Before use, all glass wares were systematically cleaned using aqua-regia (3:1 HNO_3/HCl (*v/v*)) and rinsed with DD water.

2.2. Preparation of copper oxide micro flowers

In a typical synthesis process, 0.1 M copper nitrate solution was prepared in 50 mL of DD water and mixed with 0.05 M HMTA solution prepared in 50 mL DD water under continuous stirring for about 20 min at room temperature. The resultant blue color solution was transferred to a two-necked flask and refluxed at 90 °C for 3 h by using an adjustable thermocouple in the refluxing flask. Potential hydrogen (pH) of the reaction mixture was revised to 6.0 through addition few drops of NaOH. After completion of the reaction, the solution temperature was reduced to room temperature; obtained black color CuO precipitate was washed with methanol several times and dried at room temperature [19].

2.3. Characterizations

The phase purity and crystal structure of the products were analyzed with powder X-ray diffraction patterns (XRD) recorded by a Philips XPertPro X-ray diffractometer with the CuKα radiation. The infrared spectra were recorded using Thermo Scientific Nicolet iS5 FTIR spectrometer. The morphology and size of the particles were analyzed by scanning electron microscope (SEM, JEOL 7401 F) and high-resolution transmission electron microscope (HRTEM; JEOL model JEM2010). Energy dispersive X-ray (EDX) analysis was used to determine the elements present in the nanoparticles.

2.4. Electrochemical investigation

Electrochemical measurements were carried out on a CHI 650 C electrochemical workstation (Austin, TX, USA). A conservative three-electrode system was employed for cyclic voltammetric (CV) and amperometric studies. A three-electrode electrochemical cell was employed with Ag/AgCl as the reference electrode (3 M KCl), CuO MFs accumulated glassy carbon (3 mm diameter) as the working electrode and Pt wire as the counter electrode. All the glucose sensing experiments were performed at room temperature and in 0.1 M alkaline NaOH solution.

The modified electrode was prepared as follows: Bare glassy carbon electrode was carefully polished with 1 μm, 0.3 μm and 0.05 μm alumina slurry followed by washing with DD water. Before use, the electrode was sonicated for 5 min in ethanol and then in water. As synthesized 0.1 g CuO MFs was dispersed uniformly in Nafion suspension for ~20 min of ultrasonication. 10 μL of the prepared CuO MFs suspension was spread on the GC electrode surface and dried at room temperature. The as-prepared electrode is denoted as CuO MFs/Nafion/GC. Argon was purged for 10 min to the electrolytic solution prior to the starting of electrochemical experiments.

3. Results and discussion

3.1. Structural characterizations of flower-shaped CuO

The CuO micro flowers (MFs) structures prepared through the simple solution process using aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ and HMTA at 90 °C (pH = 6.0). There was no instant precipitation, but the clear, light-blue colored solution of copper nitrate turned into turbid by the addition of HMTA. Besides, to maintain the pH value at 6.0 for the reaction, few drops of 1 M NaOH was added to the solution, which results in the blue colored precipitate ($Cu(OH)_2$). Based on this simple chemical reaction [21], initially $Cu(NO_3)_2$ reacted with NaOH and forms the blue precipitate of $Cu(OH)_2$:

$$Cu(NO_3)_2.3H_2O + 2NaOH \rightarrow Cu(OH)_2 + 2NaNO_3 + 3H_2O$$

CuO crystals were grown from $Cu(OH)_2$ at the appropriate temperature. Therefore, the formation of $Cu(OH)_2$ is very important and lead the growth of CuO crystallites based on the chemical reaction given below:

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

A small amount of NaOH was added in the reaction at the beginning time of the reaction; thus, there were insufficient OH^- ions to produce $Cu(OH)_2$ During the reaction, HMTA hydrolyzed and produced OH^- ions by the chemical reaction mentioned below [40]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

From the observed products, one can predict the realistic growth mechanism occurred for the formation of CuO MFs structures. Fig. 1 shows a schematic diagram for the step by step formation of flower-shaped structures.

The crystal phase and crystallinity were investigated by XRD analysis in the range of 20 – 70° shown in Fig. 2. The obtained XRD results of the as-synthesized product are supported well the crystallinity of CuO MFs and it might be identified to the monoclinic phase of crystals (JCPDS 05–0661). The major peaks observed at $2\Theta = 35.5°$ and 38.8° indexed as ($\bar{1}$ 11)–(002) and (111)–(200) planes, respectively. The traits for the XRD results of the CuO crystallites shown in Fig. 2 confirm the formation of pure monoclinic phase. In addition, no side products such as $Cu(OH)_2$ and Cu_2O are noticed from the pattern. The as-prepared samples were observed by Fourier Transform infrared (FT-IR) analyses (Fig. 3) shows three characteristic infrared peaks at ~412, 497 and