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Cupric oxide nanowires assembled by nanoparticles in situ with enhancing electrocatalytic oxidation of ascorbic acid

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ABSTRACT

CuO nanowires are facilely fabricated on the surface of AgCuZn alloy in situ by direct oxidation and partial reduction procedures, which shows an improved electrocatalytic activity toward ascorbic acid oxidation. The morphology shows the nanowires are assembled by CuO nanoparticles and we consider the process that the unordered spheres convert to ordered wires is due to the reduction of [1 1 0] and [$\bar{1}$ 1 1] crystal planes in CuO. Moreover, the prepared modified electrode displays a high sensitivity of 1660 μA cm^{-2} mM^{-1}, wide linear range from 0.1 μM to 3.1 mM and a low detection limit of 0.095 μmol (signal/noise = 3). Further, the sensor is also tested for anti-interferences and real samples determination, exhibiting distinguished selectivity, accuracy, and recovery. Such excellent properties are owing to the special structure of the synthesized CuO that would provide more specific surface area and enhanced activity compared with common nanowires. Hence, this work of fabricating CuO nanowires assembled by CuO nanoparticles with high performance might supply a way for facile obtain more electrochemical sensor in this structure.

1. Introduction

Ascorbic acid (AA) is widely present in food and organs [1]. It is one of the important vitamins to maintain normal physiological functions of the body [2]. It can help the construction of blood vessels, bones, collagen, and the healing of the injuries etc., [3]. So there is a great significance to detect the content of ascorbic acid in pharmaceutical, clinical, and food industry.

In published detection methods, including spectrophotometry [4], high-performance liquid chromatography (HPLC) [5], fluorescence [6], chemiluminescence [7], and electrochemical methods [1] etc., However, all of the methods have some shortcomings. For example, HPLC consumes high cost to analyze samples and maintain instrument, spectrophotometry method is lack of selectivity and long time consuming [8]. In recent years, determination of AA with chemosensor or biosensor, especially chemical modified electrodes have obtained large attention [9]. Conductometric sensors can be facile operated but often exhibit unsatisfactory properties [10]. The enzymatic sensor has high selectivity, however its shelf life is too short and various environment factors, e.g., chemical disturbances, temperature, and optical conditions, can limit the efficiency of such sensors [9,11]. Recently, electrodes modified by nanomaterials for the determination of AA have been reported [12]. The properties of modified electrode will be enhanced due to more catalytic sites on the electrode surface [9]. Among these, noble metal nanoparticles (Au, Ag, Pt, Pd, Ru etc.,) and their alloys possessed unique electrical, magnetic, optical, and catalytic characters [2]. To our knowledge, these noble metals are precious since rare global storage is easy to be poisoned by some small organic molecules [14,15]. Besides, metal oxide nanostructures using as sensing layers have attracted growing attentions of researchers for numerous merits, such as NiO [16], MnO_2 [17], CuO [18] etc.,

CuO has superior capabilities in the catalytic activity, response range, detection limits, stability, and immunity to be poisoned by some molecules [19,20]. However, it normally owns little eletroctalytic activity to AA oxidation [18,21]. Here we first report an AA sensor based on CuO nanostructures. In this paper, we find a facile method of synthesizing CuO nanowires (NWs) assembled by nanoparticles in situ via direct oxidation and partial reduction paths. The structure shows high activity towards ascorbic acid electrooxidation and the constructed sensor displays an excellent sensitivity for AA assay with a low detection limit and good selectivity. In addition, we also test the contents of AA in real samples by using our prepared sensor, which carry out favorable results, so that it possesses potential applications in practical analyses.

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2. Experimental

2.1. Materials

NaOH, H_2O_2 (30% wt.), $NaBH_4$, KOH, Citric acid, Tartaric acid, Glycerol, Glycine, AA were purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China). NaCl were purchased from Linjiang Factory (Chengdu, China). Dopamine was purchased from Alfa Aesar (Johnson Matthey Company, USA) uric acid was purchased from Acros (New Jersey, USA)

2.2. Alloy fusion

The electrode melted by Cu, Ag, Zn substance was carried out in a columnar graphite tube with length of 5 cm, diameter of 0.2 cm by intermediate frequency furnace with 400 Hz.

2.3. Fabrication of CuO nanowires

The procedures of electrode pre-treatment are described as follows: polished the surface of AgCuZn alloy by Al_2O_3 abrasive paper to smoothness, and then cleaned ultrasonically in an ethanol for 30 s. Further, after being washed by deionized water, the prepared electrode was immerged into a 15 ml aqueous solution mixed with 0.94 M NaOH and 0.24 M H_2O_2 at 40 °C for 30 min. The surface of AgCuZn alloy has become dark brown instead of the initial golden. Then heat-treatment in the muffle furnace for three hours at 300 °C is necessary in this work. Finally, 1.0 M $NaBH_4$ solution was used to reduce partially the oxide at 30 °C for 90 min.

2.4. Instrumentation

The morphology of each electrode was characterised with a scanning electron microscope (SEM) (Hitachi S-4800). The phase of composition was measured on a powder X-ray diffractometer (XRD) (DX-1000). Electrochemical properties were tested by an electrochemical workstation three-electrode system (LK9805). Electrochemical impedance spectroscopy (EIS) was obtained by Autolab (PG STAT 12 potentiostate). All the electrochemical experiments are testing in three electrode systems with our prepared modified electrode as working electrode, platinum plate as auxiliary electrode, and saturates calomel electrode as reference electrode.

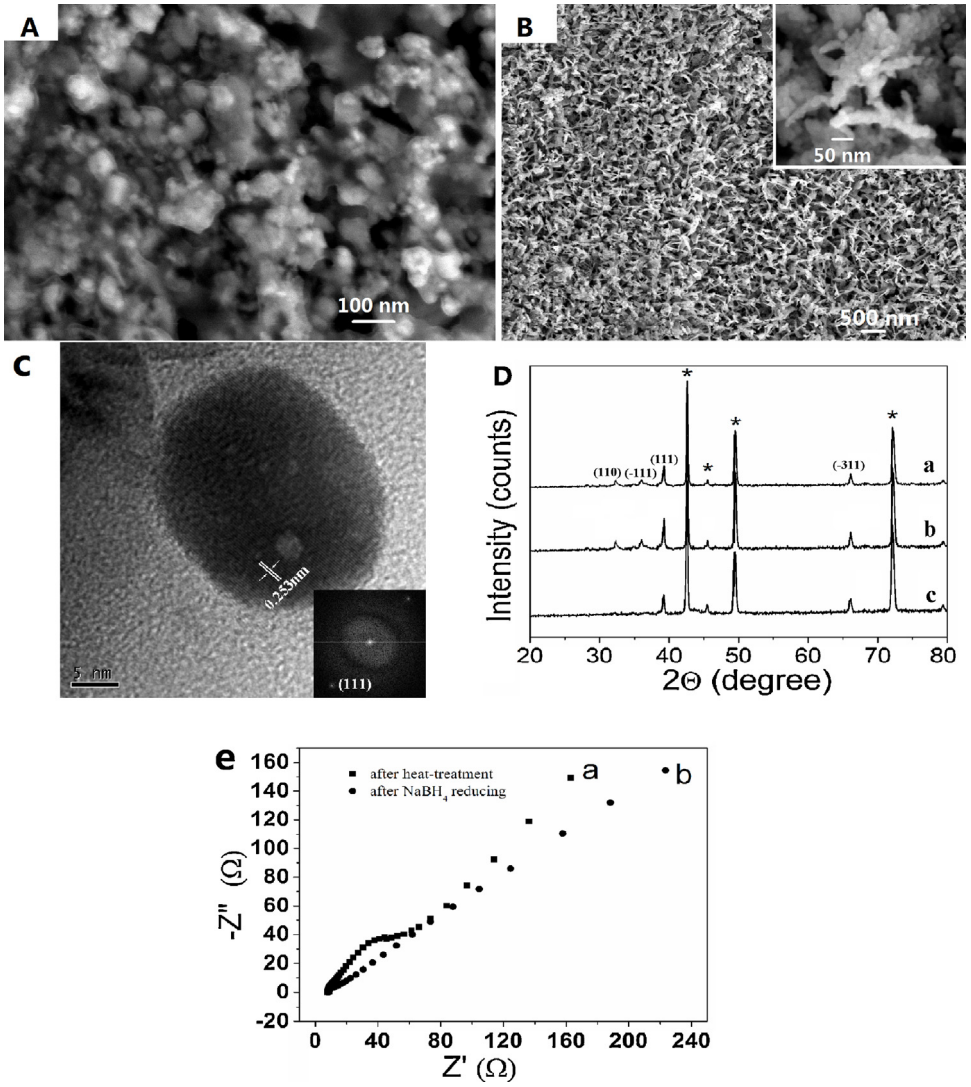

Fig. 1. (A) SEM image of electrode after heat-treatment. (B) SEM of electrode after $NaBH_4$ reducing. Scale bars: (A) 50 nm, and (B) 500 nm and inset 50 nm. (C) HRTEM image of the CuO nanoparticle on nanowire and the inset show the FFT pattern. (D) X-ray diffraction patterns of the electrodes. Curve *a* displays the patterns of electrode before (a) and after (b) heat-treatment with 300 °C for 3 h. Curve *b* shows patterns of electrode after $NaBH_4$ reducing. The sign in Fig. 1(D) are diffraction peaks of bare electrode. (E) EIS image of electrode after heat-treatment (a) and electrode after $NaBH_4$ reducing (b).