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Stable controlled growth of 3D CuO/Cu nanoflowers by surfactant-free method for non-enzymatic hydrogen peroxide detection

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ABSTRACT

Sensitive, convenient and rapid detection of hydrogen peroxide (H_2O_2) is highly desirable in fields like fundamental biological research, food industries, and clinical & environmental analysis. Herein, a hierarchical porous CuO/Cu flower-like active electrode material for non-enzymatic H_2O_2 sensor was synthesized via a low-cost and one-step chemical oxidation of Cu powder in water bath without surfactants. In order to discuss the growth mechanism of the product, products with different growth time length were fabricated. The electro-catalysis of all products were first exhibited by cyclic-voltammetry, and the product under 6 h reaction shows the best result. The detailed electro-catalytic behaviors of the best product (under 6 h reaction) are characterized by cyclic-voltammetry and amperometry under alkaline conditions. The materials have high sensitivity of 103 $\mu A\,mM^{-1}\,cm^{-2}$ ($R^2 = 0.9979$), low detection limit of 2 μmol/L and wide concentration range (from 2 μmol/L to 19.4 mmol/L). Large specific surface area and stabled nanostructure enabled good features, such as stability and sensitivity for the H_2O_2 determination.

1. Introduction

Sensitive, convenient and rapid detection of hydrogen peroxide (H_2O_2) is highly desirable in various fields including fundamental biological research, food industries, and clinical & environmental analysis [1,2]. As active electrode materials of sensors, enzymes, noble metals and transition metals are all choices under consideration. While enzymatic biosensors for H_2O_2 detection have been widely studied but its further applications are limited by chemical and thermal instabilities, limited durability, etc. [1–3]. Recently, numerous noble metals (e.g. Au [4,5] Pt [6,7], Ag [8,9], etc.) and alloys (e.g. PtAu [10,11], PtAg [12], etc.) have been studied for H_2O_2 sensors due to the excellent catalytic activities, while there are several drawbacks, such as high cost, low selectivity and toxicity, limiting their applications as sensitive materials.

Owing to narrow band gap, high electron mobility and abundant resource, the transition metal is attractive to be used for sensor, such as NiO [13,14], Co_3O_4 [15,16], MnO_2 [17], ZnO [18], and CuO [19]. Among aforementioned metal oxides, CuO, a p-type semiconductor with the narrow band gap (1.2 eV), is widely applied for catalysis, sensor, semiconductor, etc.[20–22]. For the nontoxicity, minimal cost and fast electron transfer rates resulted from the flexible switch of valence state [23,24]. So, CuO appeals to great attention for the application of H_2O_2 sensor. Besides of the intrinsic properties of copper oxides, the electro-catalytic properties of those are also extremely dependent on its nano-structural features. So varies micro/nanostructures of Cu metal (such as nano-flowers, nanocubes, and nanowires), Cu oxides, Cu sulphide and Cu-based composites have been studied to be used as active materials for hydrogen peroxide detection. For example, Banerjee et al. [25] synthesized CuO pyramidal nanostructure with MOF-199. Wu et al. [26] and Guo et al. [27] also fabricated CuO hollow structure with MOF-template. Metal oxide framework (MOF) is a good way to fabricate metal oxide with special micro/nanostructures. However, complicated and expensive fabrications hampered the development. The precise control of the process during the MOF fabrication and the structural stability of that in the subsequent synthesizing procedure are salient problems. Besides, plenty of studies preferred to add surfactants to obtain novel and special nanostructures, like nano-flowers, with high specific surface area and porosity [22,28]. But the surfactant remains in products is hard to be cleaned thor-

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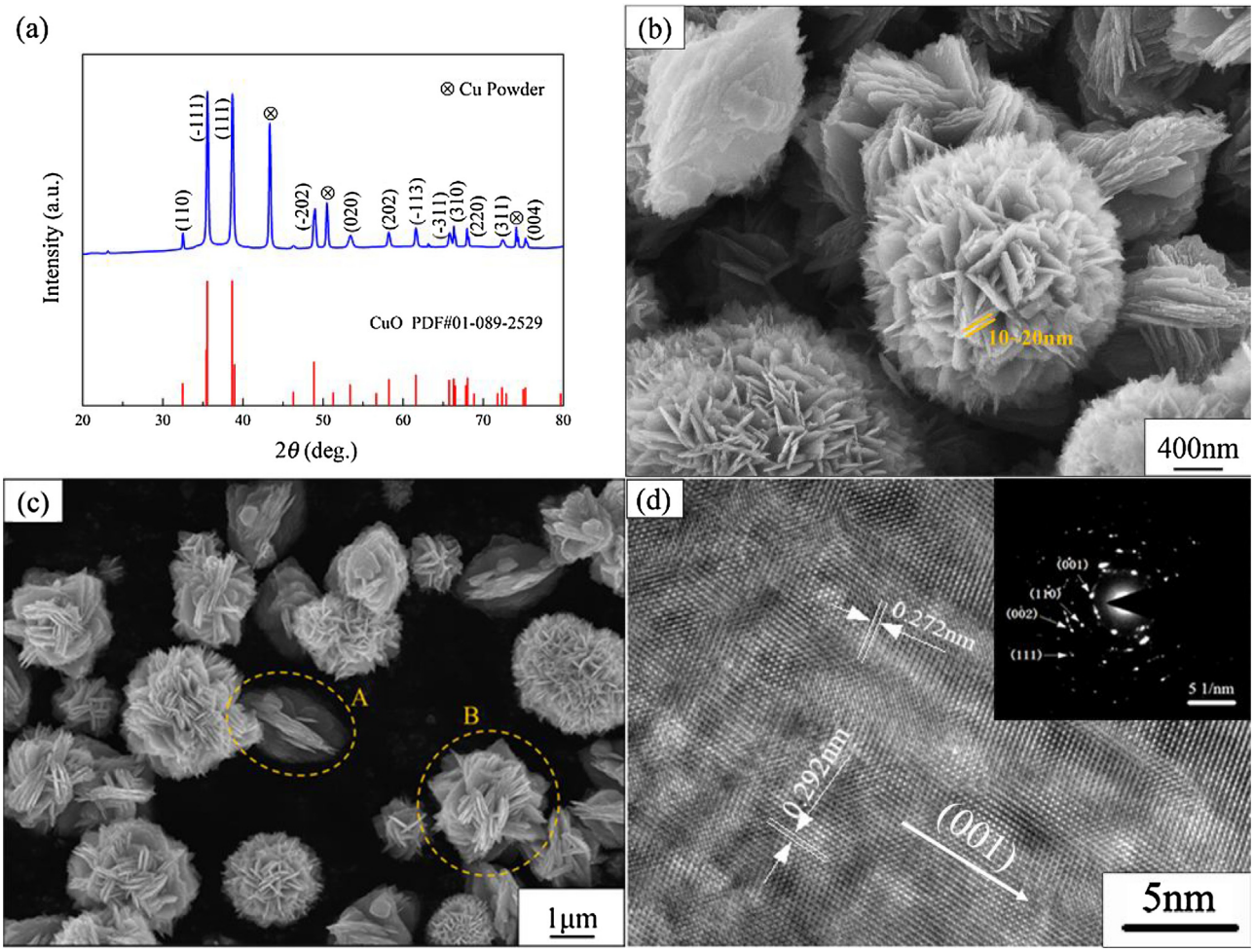

Fig. 1. (a) XRD pattern and (b, c) SEM images of the product under 6 h reaction. (d) High-resolution transmission electron microscopy (HRTEM) images of the edge of the product. Inset: the selected area electron diffraction (SAEDP) pattern of the product.

oughly, which may influence the catalytic behaviour and stability of the active material on H_2O_2 determination.

In this work, we developed a one-step surfactant-free oxidation method to manufacture hierarchical porous CuO nanoflowers. This method was performed in alkaline solution with a low-temperature and rapid-fabrication route. The final product shows outstanding sensing behaviours towards H_2O_2.

2. Experimental

2.1. Materials and methods

All the reagents were of analytical grade and used without further purification. In a typical process, 3 g sodium hydroxide and 0.68 g ammonium peroxydisulfate were dissolved in 40 mL deionized water under stirring. Then, 50 mg copper powder was dispersed into 20 mL distilled water uniformly under ultra-sonication and poured into as-obtained solution. The formed suspension was stirred in water bath for 6 h at 60 °C. The resulting black product was filtered, washed and dried at 60 °C. The products marked as CuO/Cu-6. For comparison and studying the growth mechanism of the product, the suspension was stirred in 60 °C water bath for 20 min, 80 min, 3 h and 12 h, marked as CuO/Cu-20, CuO/Cu-80, CuO/Cu-3, CuO/Cu-12, respectively.

2.2. Materials characterization

The morphologies and structures of products were identified by X-ray diffraction (XRD, X'Pert ProMPD, Cu), scanning electron microscopy (SEM, MIRA3 XMU) and transmission electron microscopy (TEM, TECNAI F-30).

2.3. Electrochemical measurements

The electrochemical measurements were carried out on a CS310 electrochemical workstation (Corrtest, China) in a three-electrode electrochemical cell with the CuO/Cu modified glassy carbon electrode as working electrode, an Ag/AgCl (saturated with KCl) electrode as reference electrode and a platinum electrode as auxiliary electrode. The cyclic voltammograms (CVs) and amperometric responses were measured in 0.1 mol/L NaOH aqueous solution at room temperature. For amperometric responses, all the measurements were carried on at an appropriate potential to the working electrode, and the background current was at steady-state values before analytes were added in.

2.4. Fabrication of modified electrode

The working electrode was made from the glassy carbon electrode (GCE) with the working area of 0.07 cm^2. Firstly, 5 mg CuO/Cu powder was added in 5 mL distilled water and ultra-sonicated to form a uniform suspension. And then, 10 μL suspension and 2 μL of