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Synthesis of Ag/γ-AlOOH nanocomposites and their application for electrochemical sensing

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ABSTRACT

Ag/γ-AlOOH nanocomposites were synthesized by employing γ-AlOOH as the support for Ag catalyst and then the nanocomposites were used for fabricating nonenzymatic H_2O_2 sensor. Transmission electron microscopy and scanning electron microscope observations reveal that large numbers of silver nanoparticles were well distributed on the surface of γ-AlOOH and the electrochemical investigations indicate that the nanocomposites possess an excellent performance toward H_2O_2. The linear range is estimated to be from 5.0 μM to 9.0 mM with a low detection limit of 1.1 μM (S/N = 3), a sensitivity of 64.4 μA mM^{-1} cm^{-2} and a response time of 3 s. These results indicated that Ag/γ-AlOOH nanocomposites were the promising electrocatalytic material for constructing sensors.

1. Introduction

Hydrogen peroxide (H_2O_2) plays critical roles in industrial, clinical and environmental analyses [1,2]. Nowadays, many techniques for determination of H_2O_2 have been reported, such as chromatography [3], chemiluminescence [4], and electrochemistry [5]. In comparison with other techniques, electrochemical sensors have been extensively applied for accurate determination of H_2O_2 [6,7]. Meanwhile, enormous research effort has been paid on the non-enzymatic sensors due to that the non-enzymatic sensors can overcome the disadvantages of enzymatic sensors, such as high cost, instability and tedious immobilization procedures [8].

Nowadays, many nanoparticles were employed to construct non-enzymatic H_2O_2 sensors, such as MoS_2 [9], CuNPs [10], MnO_2 [11] and AgNPs [12]. Moreover, recent studies indicated that AgNPs not only possessed high conductivity but also exhibited excellent catalytic activity for H_2O_2 [13]. Therefore, the non-enzymatic H_2O_2 sensors based on AgNPs keep on being of enormous current research attention. However, the strong van der Waals force between AgNPs usually causes severe aggregations, which prohibits their extensive applications [13]. Therefore, the catalyst supports which can keep the distribution of AgNPs and protect these AgNPs against agglomeration were very important. For example, Zhao [14] employed multiwall carbon nanotubes (MWCNTs) as the support for Ag catalyst and Ag/MWCNTs nanocomposites could yield high performance toward the detection of H_2O_2. Chen [15] reported that attapulgite (ATP) can be used as a matrix which facilitated the formation and homogenous distribution of small AgNPs. Some other materials, such as MnOOH [13] and Fe_3O_4 [16], were also employed as the support.

Recently, as an important adsorbent material, boehmite (γ-AlOOH) which is an aluminum oxyhydroxide has aroused growing interest due to its unique properties [17], including thermal stability, low cost, high surface area, relatively good conductivity and controllable synthesis process [18–20]. In addition, the surface of γ-AlOOH also contain large number of hydroxyl groups which can increase the number of anchoring sites for the adsorption of metal ions and therefore make γ-AlOOH inclined to interact with metal ions [17]. From the above mentioned points, γ-AlOOH can be not only used as the adsorbent but also employed as catalyst supports for the nucleation and growth of metal nanoparticles, which may facilitate the homogeneous distribution of metal nanoparticles and prohibit metal nanoparticles from aggregating. However, there are few reports about γ-AlOOH as catalyst support [21,22] and few studies have managed to support AgNPs on γ-AlOOH [23]. In addition, to the best of our knowledge, no attention has been paid to employ Ag/γ-AlOOH as an electrochemical sensor for detection of H_2O_2.

In this paper, Ag/γ-AlOOH nanocomposites were synthesized by employing γ-AlOOH as the catalyst support. Then a novel nonenzymatic H_2O_2 sensor based on the nanocomposites was fabricated and further the electrochemical performance of the sensor toward H_2O_2 was investigated.

2. Experimental

2.1. Reagents and Materials

Silver nitrate ($AgNO_3$) and potassium aluminium sulfate ($KAl(SO_4)_2 \cdot 12H_2O$) were purchased from Xi'an Chemical Reagent

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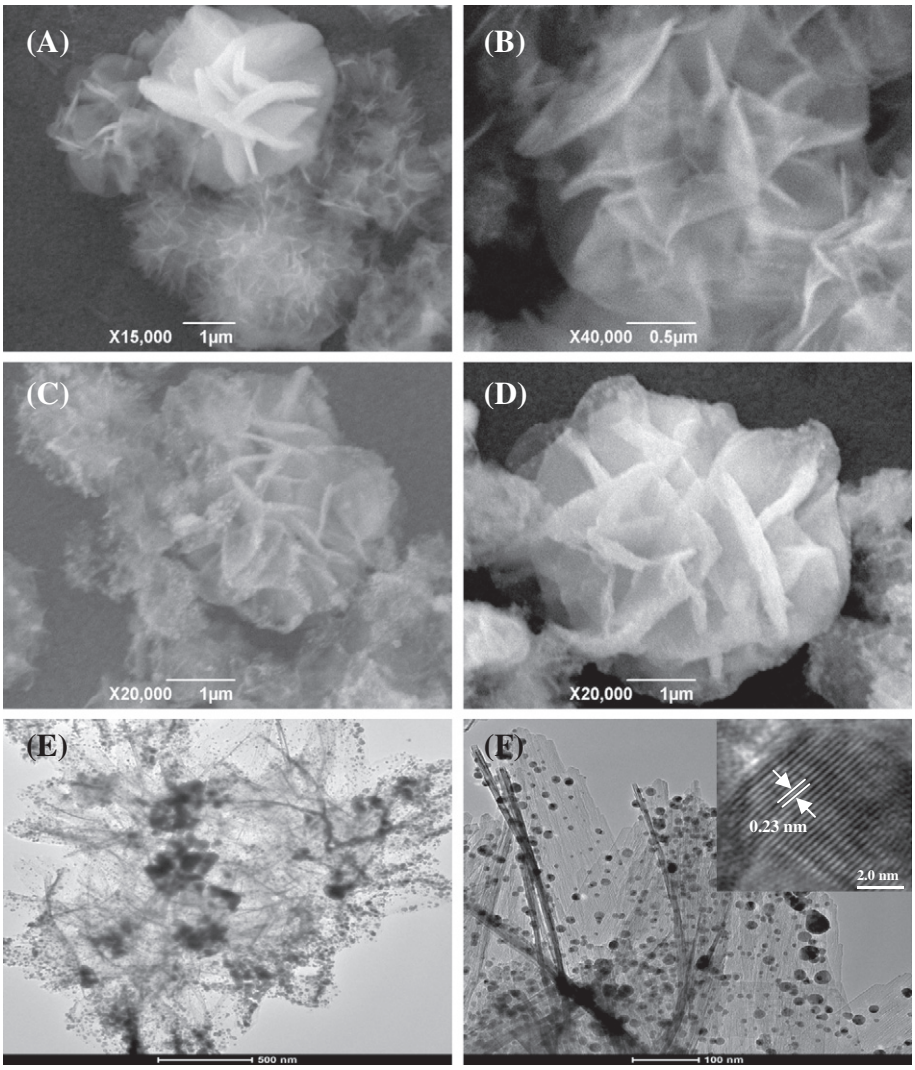

Fig. 1. SEM images of nanocomposites: (A, B) γ-AlOOH and (C, D) Ag/γ-AlOOH, TEM images of nanocomposites (E, F) Ag/γ-AlOOH.

(Xi'an, China). Urea ($CO(NH_2)_2$) was obtained from Shanghai Yuanju Biotechnology Co., Ltd (Shanghai, China). 0.1 M phosphate buffered saline (PBS, pH = 7.2) was used as the supporting electrolyte. Reagents and chemicals were of analytical reagent grade.

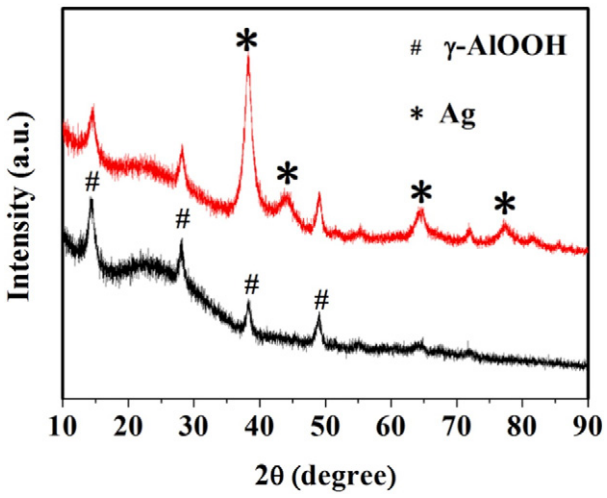

Fig. 2. XRD patterns of γ-AlOOH (black curve) and Ag/γ-AlOOH (red curve).

2.2. Apparatus

Transmission electron microscopic (TEM) images were carried out by Tecnai G^2 F20 S-TWIN (FEI, USA). Scanning electron microscopic (SEM) images were carried out by JSM 6700F (JEOL, Japan). X ray diffraction (XRD) patterns of the samples were taken by D/MAX 3C (Rigaku, Japan). Electrochemical measurements were carried out in a conventional three-electrode electroanalysis system controlled by EC 550 electrochemical workstation (Gaoss Union Technology Co., Ltd., Wuhan, China) and CHI 660 electrochemical workstation (Shanghai CH Instrument Co. Ltd., China). A conventional three-electrode cell was used, including a glassy carbon electrode (GCE, geometric area = 0.07 cm^2) as the working electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode and platinum foil as the counter electrode. All potentials given in this work were referred to the Ag/AgCl electrode.

2.3. Synthesis of Ag/γ-AlOOH

2.3.1. Preparation of γ-AlOOH

0.166 g $KAl(SO_4)_2 \cdot 12H_2O$ and 0.042 g $CO(NH_2)_2$ were dissolved in 7 ml of distilled water and stirred for 25 min. Then, the mixture was transferred into a 10 mL Teflon-lined autoclave and heated at 180 °C for a period of 3 h. After which, γ-AlOOH was separated from the solution by centrifugation at 8000 rpm for 5 min. The