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A wide linear range and stable H_2O_2 electrochemical sensor based on Ag decorated hierarchical Sn_3O_4

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ABSTRACT

Due to high electrocatalytic activity, Ag nanoparticles (Ag NPs) always be a good candidate for electrochemical sensors. However, it suffers from the aggregation problem during synthesis, storage and immobilization process. In this paper, hierarchical Sn_3O_4 was selected as scaffold for Ag NPs to prevent aggregation and ensure the stability. As a sensitive electrode to detect H_2O_2, Ag/Sn_3O_4 exhibits wide linear range and reliable stability, which can be attributed to the hierarchical structure, strong immobilization of Ag NPs and structural, physical and chemical stability of Sn_3O_4 scaffold. It was concluded that the hierarchical Ag/Sn_3O_4 architecture has potential applications in the design of nonenzymatic H_2O_2 sensors and the load of Ag NPs on heterovalent tin oxides demonstrates a promising way for building H_2O_2 detection electrodes.

1. Introduction

Fast and accurate detection of H_2O_2 is of great interests due to its important role in clinical biochemistry, pharmaceutical, food industry and environmental monitoring [1,2]. The widely used method for H_2O_2 detection is electrochemical sensors involving the use of Horseradish Peroxidase (HRP) [3–5]. Despite high selectivity of HRP, the enzymatic electrochemical sensors still suffer from the high cost and insufficient stability derived from the essence of enzyme [6,7]. Accordingly, there are widespread research interests in developing enzyme-free H_2O_2 sensors to overcome the shortage of enzyme based electrochemical sensors.

Prussian blue-based "artificial peroxidase" are considered as typical nonenzymatic electrodes to detect H_2O_2 at low potential [8–11]. However, Prussian blue-based materials are always subjected to insufficient stability. Noble metals are the widely used effective electrocatalyst due to their unique electronic configuration and excellent stability. Noble metals can decrease the overpotential of H_2O_2 during the electrocatalytic process and vast quantities of studies have focused on the noble metals-based amperometric H_2O_2 sensors [12–16]. Among the noble metals, silver nanoparticles (Ag NPs) have attracted substantial research activities due to their unique properties of biocompatibility, low toxicity, high electrocatalytic activity and sustainable price [17–19]. However, Ag NPs always tend to aggregate because of strong van der Waals force between them, resulting in a sharp decrease of electrochemical activity and stability. Thus, it is still of significant importance to construct a stable Ag-based material structure to avoid aggregation.

Immobilization of Ag NPs on organic/inorganic scaffolds was confirmed to be an effective strategy against agglomeration and improved their stability [20–22]. Thereinto, oxides have the advantage of natural abundance, environmentally benign nature and reversible electrochemical redox characteristics. In particularly, tin based oxides as important multi-functional materials have attracted lots of attentions due to their wide applications, such as sensors, catalysis, and lithium ion batteries [23–26]. Tin based oxides can be employed as the scaffold for Ag NPs because of their high chemical and physical stability, environmentally non-toxic and unique electrical property. Furthermore, tin based oxides have the characteristic of photocatalysis, which provides a green and efficient way to load Ag NPs [27]. SnO_2 and SnO with valence of +4 and +2 are the common existence status for tin based oxides. However, heterovalent tin oxides, including Sn_5O_6, Sn_3O_4 and Sn_2O_3, are taking increasing attentions and have been demonstrated to possess special performance compared to both SnO_2 and

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SnO [28–31]. The research of heterovalent tin oxides based materials is of particular interests and has been proposed for a remarkable wide range of applications.

In this paper, heterovalent Sn_3O_4 was employed as scaffold and photoreductant for Ag NPs for the first time. Inspired by the intimate correlation between structure/morphology and electrochemical performance, hierarchical Sn_3O_4 composed of nanosheets was constructed as the scaffold. The hierarchical Sn_3O_4 provides large surface area for load of Ag NPs and offers more diffusion path for analyte, which benefits the electrocatalytic kinetics during the detection. In addition, hierarchical materials afford extra inter space to accommodate the volume change and alleviate the structural strain during the electrocatalytic process, leading to an improved stability of Ag/Sn_3O_4 electrode [32]. Severed as an electrode for detection of H_2O_2, hierarchical Ag/Sn_3O_4 assumed wide linear range (up to 12.75 mM) and reliable stability. The hierarchical Ag/Sn_3O_4 architecture presents wide applications in the design of nonenzymatic H_2O_2 electrochemical sensors and the immobilization of Ag NPs on heterovalent tin oxides paves a new way to build H_2O_2 detection electrodes.

2. Experimental procedure

2.1. Preparation of hierarchical Sn_3O_4

The hierarchical Sn_3O_4 was synthesized by a one-step hydrothermal method using sodium citrate as a ligand. In a typical procedure, 0.9 g $SnCl_2{\cdot}2H_2O$ was first dissolved into 20 ml deionized water under stirring. Then 2.94 g $Na_3C_6H_5O_7{\cdot}2H_2O$ was added into the above solution. After stirring for 20 min, the suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 16 h and subsequently cooled down to room temperature naturally. The yellow products were centrifuged for several times by deionized water and dried at 60 °C overnight.

2.2. Synthesis of Ag/Sn_3O_4 architecture

Ag NPs were decorated on hierarchical Sn_3O_4 by an *in situ* photocatalytic reduction method. 0.1 g of the prepared Sn_3O_4 powers were dispersed into 100 ml $AgNO_3$ solution (25 mM) under stirring for the adsorption of Ag^+. After 1 h, the hierarchical Sn_3O_4 were centrifuged and immediately irradiated under a 365 nm ultraviolet light for 2 h to reduce the adsorbed Ag^+ to Ag. Finally, the black products were rinsed by deionized water and dried at 40 °C in vacuum for 12 h.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) and amperometric tests were performed in 0.1 M phosphate-buffered solution (PBS, pH = 7.0) on a μ3AUT71083 Autolab electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were tested with a frequency range between 0.01 Hz–100 kHz with a perturbation

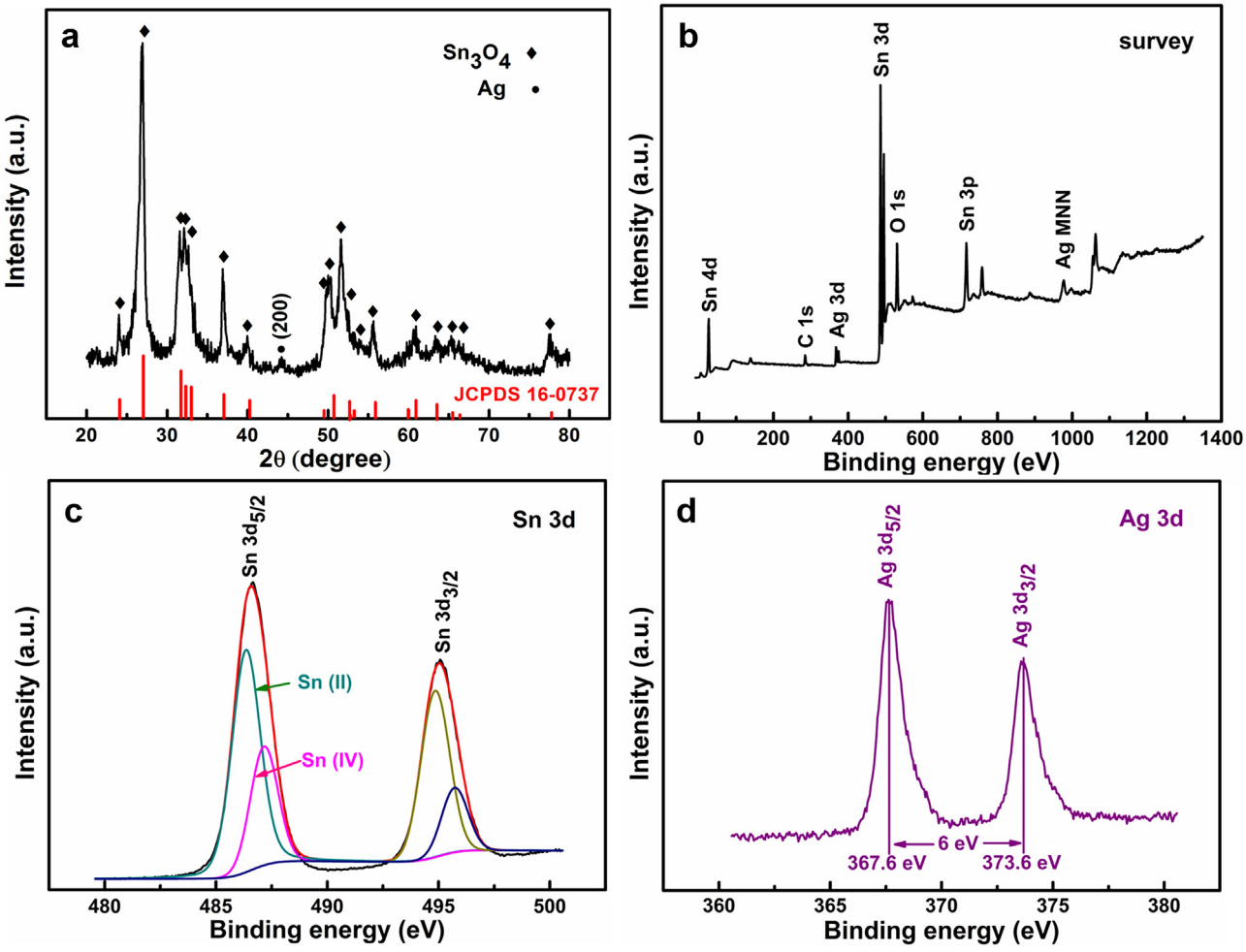

Fig. 1. (a) XRD pattern of hierarchical Ag/Sn_3O_4 architecture; XPS spectra for hierarchical Ag/Sn_3O_4 architecture. (b) Survey; (c) Sn 3d; (d) Ag 3d.