Electrochimica Acta 217 (2016) 139–149

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Microwave assisted growth of stannous ferrite microcubes as electrodes for potentiometric nonenzymatic H_2O_2 sensor and supercapacitor applications

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ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form 16 September 2016
Accepted 16 September 2016
Available online 17 September 2016

Keywords:
Stannous ferrite
Microwave assisted method
Hydrogen peroxide sensor
Supercapacitor
Electrochemical performance

ABSTRACT

Electrochemical sensors and supercapacitors are two noteworthy applications of electrochemistry. Herein, we report the synthesis of $SnFe_2O_4$ microcubes and Fe_2O_3 nanorods through a facile microwave assisted technique which are employed in fabricating the electrodes for nonenzymatic hydrogen peroxide (H_2O_2) sensor and supercapacitor applications. $SnFe_2O_4$ microcubes exhibited an enhanced specific capacitance of 172 Fg^{-1} at a scan rate of 5 mVs^{-1} in comparison to Fe_2O_3 nanorods (70 Fg^{-1}). Furthermore, the H_2O_2 sensing performance of the fabricated $SnFe_2O_4$ electrodes through chronopotentiometry studies in 0.1 M PBS solution (at pH 7) with a wide linear range revealed a good sensitivity of 2.7 mV μM^{-1} μg^{-1} with a lowest detection limit of 41 nM at a signal-to-noise ratio of 3. These results indicate that $SnFe_2O_4$ microcubes are excellent materials for the cost effective design and development of efficient supercapacitors as well as nonenzymatic sensors.

1. Introduction

Transition metal oxides are one of the most fascinating class of materials among inorganic solids owing to the multitude of properties they exhibit and their cost effective scalable synthesis [1]. Spinel ferrites of the form MFe_2O_4 (M = Co^{2+}, Ni^{2+}, Mn^{2+}, Sn^{2+}, etc.) are a small group of transition metal oxide compounds that are primarily derived from magnetite (Fe_3O_4). The unique electrical and magnetic properties of spinel ferrites have attracted a wide range of applications such as high-density data storage, heterogeneous catalysis, optical limiting, sensors, spintronics, magnetocaloric refrigeration, magnetic labeling in immunoassays, guided drug delivery, magnetic resonance imaging and hyperthermia of cancer cells [2–10].

Spinel ferrites have also been utilized for applications in electrochemistry such as lithium ion batteries, supercapacitors, electrochemical sensors, etc. [11–14]. Supercapacitors are electrochemical capacitors with high power density and fast charge-discharge performances that are essentially important for reducing the global reliance on exhaustible natural resources and curbing their environmentally hazardous pollutants. Pseudo-capacitors (redox capacitors) are the subcategories of supercapacitors, in which the active material undergoes redox reactions and enhances the specific capacitance of the supercapacitor [15]. On the other hand, electrochemical sensors are significantly important for biomedical applications such as the detection of various analyte molecules such as hydrogen peroxide, glucose, dopamine etc. [13,16]. Among electrochemical techniques, chronopotentiometry is one of the promising techniques in which the change in concentration of the additive results in potential drifts that can be calibrated and used for the sensing applications. Potentiometric sensors usually have the wide linear range and lower limit of detection [17–19].

Amidst many different analytes, detection of hydrogen peroxide (H_2O_2) is significantly important owing to its usage in various fields such as environmental, food, pharmaceutical, clinical analysis and biological processes. Among various techniques of H_2O_2 detection such as spectrometry, tritimetry, chemiluminescence and electrochemical, the electrochemical approach is the most accurate, fast and cost effective [20–22]. Electrochemical detection approach can be subdivided into two categories *viz.*, enzymatic and nonenzymatic. Though enzymatic approach is capable of detecting relatively low concentrations of H_2O_2 with good sensitivity, they are a failure due to the expensive cost of enzymes, their instability and challenging immobilization process. The failures of enzymatic

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http://dx.doi.org/10.1016/j.electacta.2016.09.083
0013-4686/

sensors have been successfully addressed through nonenzymatic sensors fabricated using various materials on modified electrodes. However, obtaining very high sensitivity together with lowest detection limit on modified electrodes is a challenging task.

Spinel ferrites and their composites can potentially electrocatalyze the reduction of H_2O_2. The stable spinel structure of ferrites contributes the solid state redox couples like M^{3+}/M^{2+} and Fe^{3+}/Fe^{2+} enables their active participation in the electrochemical reaction for increasing the rate of electron transfer [23–25]. The lower redox potential of Sn in stannous ferrite ($SnFe_2O_4$) is expected to provide Sn^{4+}/Sn^{2+} along with Fe^{3+}/Fe^{2+} as redox couples for effectively catalyzing the reduction of H_2O_2, which suggests that $SnFe_2O_4$ is a promising material for electrochemical applications. In this context, the main aim of the present work is to synthesize $SnFe_2O_4$ through a simple approach and explore its application as electrodes for supercapacitors and nonenzymatic sensors. Also, to the best of our knowledge there are no reports available in the literature on the synthesis of $SnFe_2O_4$ through microwave assisted approach and its applications in supercapacitors or sensors. In this regard, herein we fabricated $SnFe_2O_4$ based electrodes from the powders obtained by the microwave treatment of precursors ($FeCl_3$ and NaOH) along with $SnCl_2$, which interestingly gave rise to a microcube like morphology. Electrochemical analysis through cyclic voltammetry indicated a specific capacitance of the 172 Fg^{-1} for $SnFe_2O_4$ which was almost three times higher in comparison to Fe_2O_3 (70 Fg^{-1}) at a scan rate of 5 mVs^{-1}. Furthermore, $SnFe_2O_4$ electrode worked as an excellent sensor for the nonenzymatic detection of H_2O_2 and the calculated lower detection limit for $SnFe_2O_4$/GCE (41 nM) was three orders of magnitude lower than that of Fe_2O_3/GCE (0.3 μM).

2. Experimental

2.1. Microwave assisted synthesis of $SnFe_2O_4$ microcubes and Fe_2O_3 nanorods

All chemicals used for synthesizing the samples were of analytical grade procured from *Merck*, used directly without any further purification. In a typical synthesis, 100 mM $FeCl_3{\cdot}6H_2O$ dissolved in 100 ml of doubly distilled water was mixed with 100 ml solution of 50 mM $SnCl_2{\cdot}2H_2O$ under continuous stirring at room temperature. Thereafter, NaOH flakes were directly added for increasing the pH of the solution to 13 and it was kept under constant magnetic stirring for 30 min. The final reaction mixture was placed inside a microwave oven and was reacted at a power of 180 W for 5 min. After microwave treatment, the solution was allowed to cool down to room temperature after which it was centrifuged by repeatedly washing the precipitates with excess distilled water and acetone. The washed precipitates were dried at 60 °C for 12 h and were annealed at 600 °C for 10 h in a muffle furnace. The final $SnFe_2O_4$ sample obtained after annealing were brownish black colored powders.

Fe_2O_3 nanorod samples were prepared by following the same procedure as mentioned above without the addition of $SnCl_2{\cdot}2H_2O$. The precipitates of Fe_2O_3 obtained after annealing at 600° C for 10 h were orange red in color.

2.2. Characterization

Structural properties of the prepared samples was analyzed using an X-ray diffractometer (XRD, *Rigaku miniflex 600 XRD instrument*) at the scan rate of 2°/min with a step size of 0.02° in the 2θ range 10-80°. Morphology and the compositional analysis were conducted using a field emission scanning electron microscope (FESEM, *ZIESS*) fitted with an energy dispersive X-ray spectrometer (EDS). Fourier transform infrared (FTIR, *Bruker Alfa FTIR spectrometer*) spectra were recorded from 400 to 4000 cm^{-1} using KBr pellet. Thermal studies using both thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) were conducted on a TGA-DSC (*DSC SDT Q600*) system under nitrogen atmosphere by heating the samples from room temperature to 800 ° C. The specific surface area, pore volume and pore diameter of the samples were evaluated using the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption-desorption isotherms obtained using a BELSORP mini II instrument (*BEL Japan Co., Ltd*).

2.3. Preparation of supercapacitor electrodes and electrochemical characterization

Working electrode of the supercapacitor was fabricated using a slurry prepared by thoroughly mixing the active material (Fe_2O_3 or $SnFe_2O_4$), super P acetylene carbon black and polyvinylidene fluoride (PVDF) in the weight ratio of 7:2:1 with a few drops of N-methyl-2-pyrrolidone (NMP), which was brush coated on a pre-cleaned titanium foil (*Alfa Aesar*, 0.25 mm thickness and dimension 5×1 cm) and dried in a vacuum oven for 15 h at 60 ° C. The average mass of the active materials coated on the foil was 0.35 mg. Electrochemical studies were conducted on a *Biologic SP-150* electrochemical workstation with three-electrode system using the sample coated titanium foil, platinum wire and Ag/AgCl as the working electrode, counter electrode and reference electrode, respectively. The electrochemical properties were characterized through cyclic voltammetry (CV, at different scan rates), galvanostatic charge-discharge (GSD) method and potentiometric electrochemical impedance spectroscopy (EIS) at a bias voltage of 10 mV in three different aqueous electrolytes *viz*., 1 M KOH, 1 M NaOH and 1 M Na_2SO_4.

2.4. Preparation of electrodes for nonenzymatic H_2O_2 sensor and its measurement

In a typical procedure, a glassy carbon electrode (GCE) was cleaned by polishing its surface with alumina (0.05 μm) followed by electropolishing in 0.5 M H_2SO_4 and sonicating in distilled water and ethanol for 5 s each. A homogeneous slurry was prepared by sonicating 1 mg of sample (Fe_2O_3 or $SnFe_2O_4$) in 1 ml of NMP for 1 h after which 4 μl was drop casted using a micro pipette on the polished GCE surface (3 mm diameter). The modified GCE was dried and used as the working electrode for sensing H_2O_2 on a *Biologic SP-150* electrochemical work station with three-electrode configuration against Ag/AgCl electrode. Pt wire was used as counter electrode in 0.1 M phosphate buffer saline (PBS) solution (pH 7) as electrolyte. H_2O_2 sensing performance was analyzed using CV at the scan rate of 50 mVs^{-1} and by chronopotentiometry at an applied current of 0.4 μA in 0.1 M PBS solution.

3. Results and discussion

3.1. Structural, chemical and morphological characterization of Fe_2O_3 and $SnFe_2O_4$

XRD patterns of Fe_2O_3 and $SnFe_2O_4$ shown in Fig. 1a and 1b were analyzed and indexed using *Panalytical Xpert high score plus* software. XRD peaks of Fe_2O_3 can be indexed to the rhomboheadral structure of hematite (JCPDS card no. 01-089-0596) while the XRD pattern of $SnFe_2O_4$matched well with the phase pure monophasic inverse spinel structure (JCPDS card no. 01-071-0693) with a lattice constant of 8.4 Å [26]. However, the XRD patterns of as-synthesized precipitates of Fe_2O_3 as well as $SnFe_2O_4$ before annealing at 600 °C exhibited discrete phases (see Fig. S1, supplementary content). This indicates that Sn (in the form of Sn^{4+}) ions enter the octahedral sites by replacing Fe^{3+} ions only