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Cathodic and anodic deposition of FeS_2 thin films and their application in electrochemical reduction and amperometric sensing of H_2O_2

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ABSTRACT

A comparative study has been made on the performance of electrochemical reduction and amperometric sensing of H_2O_2 by the cathodically and anodically deposited orthorhombic FeS_2 thin films. Individual chronoamperometric depositions were carried out on indium doped tin oxide (ITO) coated glass substrates from an aqueous solution containing Mohr's salt ($FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$) and $Na_2S_2O_3$ with optimized molar concentrations. Cyclic voltammetry and linear sweep voltammetry were carried out to determine the exact reduction and oxidation potentials for the two systems. Structural, morphological, compositional, optical and electrical characterizations were carried out using X-ray diffraction (XRD) technique, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), UV–vis spectroscopy and four-probe and two-probe current–voltage measurements, respectively. It was established from XRD that both cathodic and anodic depositions were orthorhombic (Fe:S = 1:2) in nature. Cathodic films were found to have interlinked fiber like morphology, while the anodic films showed flake-like and rough morphology. It was also observed that the amperometric sensing mechanism was highly dependent on the morphology of the deposited films.

1. Introduction

FeS_2 has gradually become known for its good electrocatalytic and photocatalytic activities [1–4] toward several pollutants like organic dyes and peroxides, etc., mainly due to its nontoxicity, low cost of fabrication, abundance of the raw materials in nature and excellent electron mobility. The high optical absorption coefficient also ($\alpha \geq 10^5\ cm^{-1}$) helps the material to act as a good photocatalyst. Several techniques have been developed to synthesize FeS_2 thin films like, chemical spray pyrolysis (CSP) [5,6], chemical vapor transport (CVT) [7], metal organic chemical vapor deposition (MOCVD) [8,9], sulfurization of iron oxide (SIO) [10], ion plasma assisted sulfurization [11], magnetron sputtering [12], argon and reactive sputtering [13], screen printing [14], sulfurization of electrodeposited iron films [15], molecular beam deposition [16], etc. According to the knowledge of the authors, literature shows very little previous work on the electrocatalytic activity of the electrodeposited of FeS_2 thin films, though, there are several advantages of this technique like, uniform large area deposition, less wastage of material, minimum energy requirement, etc. Pimenta et al. [17] prepared FeS_2 thin films by sulfurization of electrodeposited iron films. Nakamura and Yamamto [18] also prepared FeS_2 thin films by sulfurization of electrodeposited FeS thin films.

Here, we report in detail the electrochemical behavior for the cathodic and anodic deposition of FeS_2 thin films on indium doped tin oxide (ITO) coated glass substrates. We have also shown the morphology dependent amperometric sensing characteristics for the two types of films.

2. Experimental

2.1. Deposition procedure

The working solution was prepared taking 10 mL 0.1 M $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ (AR grade), 10 mL 0.1 M $Na_2S_2O_3$ (AR grade) and 80 mL double distilled water. The optimum pH and temperature were found to be 5.2 and 80 °C, respectively, for both cathodic and anodic deposition of FeS_2 films. Properly cleaned ITO coated

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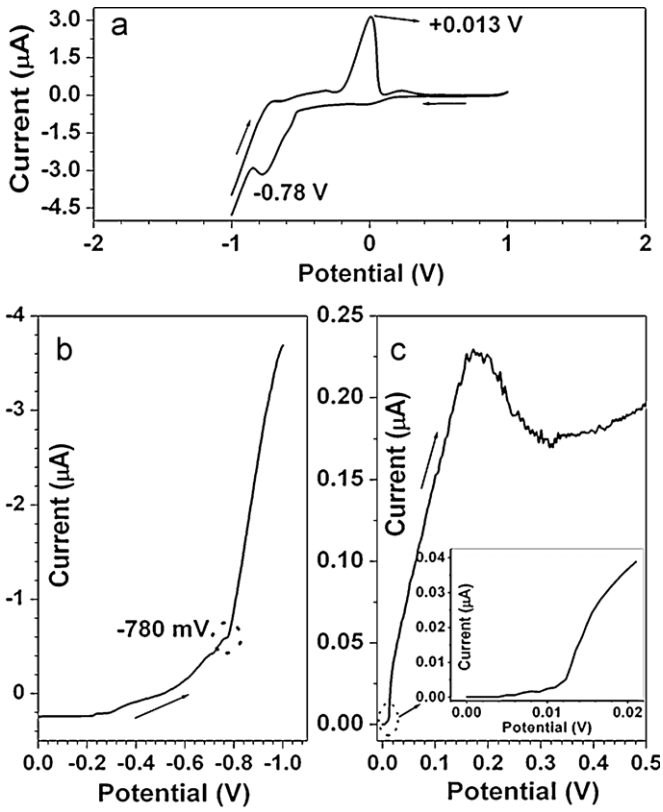

Fig. 1. (a) CV and (b, c) LSV curves showing the oxidation-reduction potentials for the working solution containing 10 mL 0.1 M $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$, 10 mL 0.1 M $Na_2S_2O_3$ and 80 mL double distilled water at pH 5.2 and 80 °C temperature. The scans were done using Pt foil and Ag/AgCl electrode as the counter and reference electrodes, respectively, in a three electrode system within the range −1.0 V to +1.0 V, at a scan rate of 0.05 V/s and sensitivity (A/V) 0.1. Inset of figure (c) is showing the magnified view of the LSV curve within 0.00 V to 0.02 V.

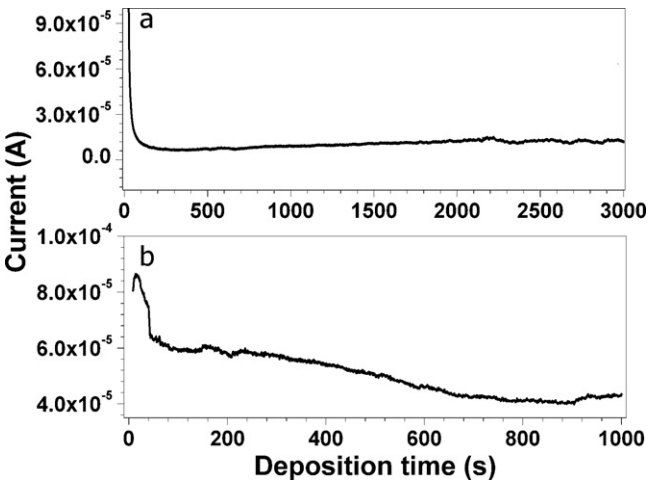

Fig. 2. Chronoamperometric curves for the (a) cathodic and (b) anodic depositions.

glass substrates were used as the working electrodes (cathode and anode), whereas, Pt foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively in a three electrode system. For proper cleaning of the ITO coated glass substrates, at first, they were washed with commercially available liquid detergent and then were put into concentrated chromic acid solution for about 20 min and washed thoroughly with cold distilled water to remove any adhering impurities. After that, they were boiled in methanol to remove any organic impurities and then were held in the vapor of trichloroethylene to make them degreased. The polished ITO substrates (XY10S) were purchased commercially from 'XINYAN Technology Limited', Hong Kong, with a resistance of 10 Ω/sq, thickness of the conducting layer being 180 nm and transparency around 83% at 550 nm. Cyclic voltammetric (CV) scan was carried out with the working solution (Fig. 1a) for the determination of exact position of the oxidation/reduction peaks in the system. The CV scan was done within the range −1.0 V to +1.0 V, with a scan rate of 0.05 V/s and the sensitivity (A/V) was 0.1. From Fig. 1a, a distinct oxidation peak was observed at a potential of 13 mV and with a peak current (I_p) of 3.108 μA. In the negative scan region, the reduction peak was found to appear at −780 mV with an I_p of −3.153 μA. We have checked the reproducibility of the redox response by CV by varying the scan rate from 0.05 V/s to 0.20 V/s with an interval of 0.05 V/s and found no significant change in the redox system, which indicates high reproducibility of the process. In order to confirm the positions for the oxidation and reduction peaks, linear sweep voltammetry (LSV) was carried out. For the cathodic sweep, the ITO coated glass was served as the cathode, while a Pt and an Ag/AgCl electrode acted as the anode and reference electrodes, respectively. For anodic sweep, the ITO glass was taken as the anode, keeping the counter and reference electrodes as usual. The cathodic sweep was performed from 0.0 V to −1.0 V, with a scan rate of 0.05 V/s and sensitivity (A/V) of 0.01 and shown in Fig. 1b, from which, a sharp rise in current was observed around −780 mV, indicating the onset of the cathodic reduction and subsequent deposition of the film on the ITO glass. On the other hand, the anodic sweep (Fig. 1b) was done from 0.0 V to 500 mV with the same scan parameters as the cathodic sweep. From Fig. 1c (inset), a sharp rise in current was observed at around 13 mV, indicating the onset of the anodic deposition. The threshold potentials as obtained from LSV curves for both cathodic and anodic depositions match well with the reduction and oxidation potential values, respectively, as obtained from CV. In order to prepare films for physical characterization and applications, chronoamperometric (CA) depositions were carried out at pH 5.2, with constant stirring the working solution at 500 rpm and at a temperature of 80 °C. For the cathodic deposition, a fixed potential of -800 mV was applied for 3000 s (Fig. 2a), while, for the anodic deposition, a constant potential of 200 mV was applied for 1000 s (Fig. 2b), so that, the films come out with good surface coverage and comparable thickness. The film thickness was determined gravimetrically and found to be about 1.8 and 1.7 μm, respectively for the cathodic and anodic films. In the gravimetric method, first, the weight of the properly cleaned and dried blank substrate (TCO coated glass), chosen for deposition, was taken using a Mettlar Balance (AB54-S) with an accuracy of 0.1 mg. After thorough wash and drying of the deposited films, they were weighed, while the length and breadth of the coatings were measured by using a Vernier Scale to determine the surface area. The density of the material was then applied to calculate the thickness of the deposited films with the help of the following equation:

$$t = \frac{(W_2 - W_1)}{Ad}$$

where, t is the thickness of the deposited film, W_1 is initial weight, i.e. the weight of the blank substrate, W_2 is the final weight, i.e. the weight of substrate with film, A is the area of deposition and 'd' is the density of the deposited film, for FeS_2 which is 4.7 g/cc.

For cathodic and anodic depositions, we propose the following two different mechanisms:

For cathodic deposition:

$$Fe^{2+} + 2e \rightarrow Fe^0 \quad (E^0 = -0.41\,V) \qquad \text{(i)}$$