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Electrochemical and fluorescence properties of SnO_2 thin films and its antibacterial activity

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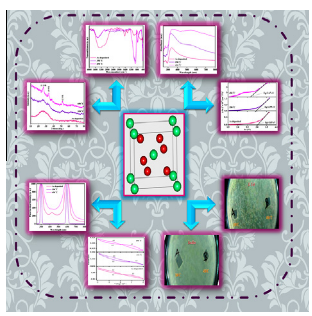
HIGHLIGHTS

- Synthesis of SnO_2 thin films by spin coating method.
- The as-deposited films were annealed at 350 °C and 450 °C.
- The effect of annealing temperature on fluorescence and electrochemical properties of the films were analyzed.
- For the first time the fluorescence property of SnO_2 thin films has been studied.
- All film shows antibacterial activity against *E. coli* and *Bacillus*.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanocrystalline SnO_2 thin films were deposited by a simple and inexpensive sol–gel spin coating technique and the films were annealed at two different temperatures (350 °C and 450 °C). Structural, vibrational, optical and electrochemical properties of the films were analyzed using XRD, FTIR, UV–Visible, fluorescence and cyclic voltammetry techniques respectively and their results are discussed in detail. The antimicrobial properties of SnO_2 thin films were investigated by agar agar method and the results confirm the antibacterial activity of SnO_2 against *Escherichia coli* and *Bacillus*.

Introduction

Nanometer sized SnO_2 thin film has engrossed considerable interest now-a-days due to their fascinating electrical and chemical properties. It is a wide band gap n-type semiconductor with unique properties, including high electrical conductivity, high thermal stability, high transmittance at near IR and visible wavelengths. These properties make SnO_2 thin film useful for functional applications such as, transparent conductive electrodes in solar cell, flat panel displays and gas sensors [1–3] in which, the conductivity of SnO_2 is low in air, but it markedly increases when the air is mixed with a reducing gas (H_2, CO and organic molecules). Hence it is used for sensing gas and alcohol applications [4–5]. Apart from these, SnO_2 is used as an anode material for rechargeable Li-ion batteries [6], self cleaning application [7], anti reflection coatings [8] and its antibacterial behavior help to protect underwater optical instruments against biofilms in seawater as well as act as electrodes for oxidation of chloride ions [9].

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Köse et al. [10] reported that, the SnO_2 film can be used as a good anode, and cost effective candidates for Li-ion batteries. Jana et al. [11] found that Pt-SnO_2 films have high current density and better stability; hence it can be used as an active material for the electrodes. In most of the reports, the authors have studied its structural, optical, electrical properties of SnO_2 by XRD, SEM, AFM, UV–Vis and Photoluminescence [1–21]. In recent years, optical properties of nanocrystalline SnO_2 are a subject of great interest. Lekshmy et al. [22] have reported that the high temperature annealing of SnO_2 increases the crystallinity and oxidation process. Hence, it decreases the defects and reduces the traps for non-radiative transition and the intensity of Photoluminescence (PL) increases with increase in annealing temperature. Kasem [23] suggested that, the oxygen vacancies interact with interfacial tin vacancies and lead to the formation of a considerable amount of trapped states within the band gap, which results in a strong Photoluminescence signal. Woo et al. [24] have reported structural characteristic of SnO_2 films deposited by spin coating method. Up to now, most of published articles were related to only structural and optical properties of SnO_2 films [1–23] but there is paucity of information on fluorescence properties of SnO_2 films. This technique provides in-depth knowledge about vacancies exist in SnO_2 films. Hence, it is motivated to analyze the fluorescence properties of nanostructured SnO_2 films. This study investigates the optical, fluorescence, electrical properties of SnO_2 films.

The researchers have prepared SnO_2 thin films by variety of preparation techniques such as spray pyrolysis [12], chemical bath deposition [13], vapor deposition [14], atmospheric pressure chemical vapor deposition [15], atomic layer deposition [16], DC-magnetron sputtering [17], RF sputtering [18], pulse laser deposition [19] and sol gel method [20,25]. Among them, the sol gel method has certain privileges namely: (i) ability to obtain ultra fine films, (ii) easy coating at a large area on non flat and complex shaped substrates, (iii) low cost and simple with non sophisticated equipments, (iv) films obtained in both thin and thick forms with high porosity area, thereby offering improvement in device fabrication. The most significant advantage of sol gel is, the films are obtained under low temperature process and preparation parameters are easily controlled which leads to high quality SnO_2 layers.

In sol gel method solution or sol is used for coating. There are three kinds of methods for applying sols to the substrate: dip coating, spin coating and laminar flow coating. In dip coating the substrate is immersed in a dipping solution and is drawn up vertically. The solution dragged by the substrate is solidified into a gel. In spin coating, an amount of solution is propped in the rotating substrate and converting it to sol film. The sol film formed becomes solidified as a gel film. In the laminar flow method a substrate is coated in an upside-down position. The coating solution is pumped into a slot applicator tube and flows out to the surface through the slot, forming continues liquid film so that narrow meniscus created between it and the applicator tube. As the applicator is moved horizontally relative to the substrate, a liquid film is left on the substrate. In all these methods films formed after evaporation of the solvents. Among the three kinds, spin coating has many advantages such as low cost, simple deposition equipments, easier adjustment of composition. Especially, it is suitable for the fabrication of multi-component metal oxide thin films.

Hence in this work, we aimed to analyze fluorescence and electrical properties of the SnO_2 thin films by a low cost non vacuum spin coating technique and to study the antibacterial activity against *Escherichia coli* and *Bacillus*.

Materials and methods

In this work, the precursor $SnCl_2{\cdot}2H_2O$ (AR grade) and the solvents 2-methoxyethanol and Monoethanolamine (MEA) were used. The sol was prepared by dissolving (0.5 mol L^{-1}) $SnCl_2$ in 10 ml 2-methoxyethanol. Then the mixture was stirred at 60 °C for 10 min. Consequently 0.3 ml MEA was added drop by drop to the solution to obtain gel. Subsequently the colorless solution turns into white gel, then to brown color. The solution was stirred again at 60 °C for 2 h and finally brown color homogeneous solution was obtained. The substrate cleaning procedure was adapted to the standard procedure reported elsewhere [26]. Before coating, the cleaned glass substrate was kept at 120 °C for 5 min in an oven. A drop of sol was spun on a piece of substrate, which was rotating at a speed of 3000 rpm for 30 s under room temperature. The solvent evaporation was performed at 200 °C for 5 min. The two step coating and evaporation process was repeated for 10 times so as to get a 10 layered film of the desired thickness. The films were then annealed at 350 °C and 450 °C for 1 h and then cooled to room temperature. The film thickness was determined by using the standard procedure [27,28]. The average thickness of the films was found about 171 nm.

The structural, vibrational and optical properties of the SnO_2 films were characterized by using X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and UV–Visible (UV–Vis) spectroscopy. The XRD measurements were performed by a PANalytical X'Pert Pro Powder diffractometer, with the Cu Kα monochromatic radiation source (λ = 1.5406 Å) in the range of 2θ = 10–80°. The FTIR spectra of the samples were recorded in the range of 4000–400 cm^{-1} using JASCO 6300 spectrometer. The spectral transmittance and absorbance of the SnO_2 films were recorded as a function of wavelength, in the range of 300–800 nm, using JASCO UVIDEC – 650 UV–Vis spectrophotometer. The room temperature fluorescence spectra were recorded by using a Spectrofluorometer Perkin Elmer Model-LS45. Electrochemical measurements were performed in a three electrode system (CH Instruments 680) consisting of SnO_2 as working electrode, platinum wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The buffer solution for the electrochemical measurements is composed of sodium dihydrogen phosphate and disodium hydrogen phosphate. The pH of the buffer solution was 7.

Antibacterial test

The antibacterial activity of the SnO_2 films against the bacteria *E. coli* and *Bacillus* were studied by agar agar method. A 1.3 g of nutrient broth was dissolved in 100 ml of distilled water in a conical flask. The nutrient broth solution and two test tubes were sterilized in a sterilization chamber and placed in a UV chamber to destroy the microbial contamination. The sterilized test tubes were filled with 10 ml of the nutrient broth solution, (which is taken from the conical flask) in which *E. coli* and *Bacillus* inoculated from its mother culture, which was grown in the Department of Biotechnology, Manonmaniam Sundaranar University, Tirunelveli. The cultured test-tubes were closed tightly with cotton and placed in an incubator for 12 h. This is called 12 h culture or subculture.

1.3 g of nutrient agar and 2 g of agar agar were dissolved in 100 ml of distilled water in a conical flask. The agar media, samples (SnO_2 thin films) and necessary petri dishes were sterilized in a sterilization chamber and placed in a UV chamber to destroy the microbial contamination. 15 ml of agar media was transferred to the petri dishes and allow it to solidify. The species from the subcultures were inoculated to the petri dishes by cotton swap. After swap the sterilized samples were placed in the petri dishes. The petri dishes are incubated in 37 °C for 24 h.

Results and discussion

Fig. 1(a–c) shows the XRD pattern obtained for as deposited SnO_2 and annealed thin films. The result shows that there is no