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RESEARCH ARTICLE

Fabrication and characterization of SnO_2 and SnS_2 nanobiosensor in the Presence of Aspergillus Niger Fungi

Reihane Etefagh[1, 2], Mino Alizade Pirposhte[1, 3], Rahil Radfar[1]*, Elahe Azhir[1, 2], Nasser Shahtahmasebi[1, 2], Elahe Tabasi[4]

[1]*Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran*

[2]*Nano Research Center, Ferdowsi University of Mashhad, Iran*

[3]*Angstrom Thin Film Research Laboratory Department of Physics, faculty of sciences, FUM, Mashhad, Iran*

[4]*Department of Biology, Faculty science, Ferdowsi University of Mashhad, Iran*

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ABSTRACT

In this paper, SnO_2 and SnS_2 thin films were synthesized by spray pyrolysis method on glass substrate. The synthesized films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Aspergillus Niger (A. Niger) fungi were grown in an appropriate medium and were exposed to the synthesized SnO_2 and SnS_2 thin films in a closed glass vessel to measure their nano-biosensing properties. The nano-biosensitivity of the prepared samples was investigated by studying the change in their electrical resistance at different times and temperatures happening due to the produced gases from A. niger fungi. Furthermore, the effects of humidity and CO_2 on the sensitivity of the samples were investigated in the presence of Silica-gel and $CaCo_3$, respectively. The results showed a considerable and detectable electrical resistance change for prepared samples in the presence of A. niger fungi, which supports our proposed system as a nanobiosensor.

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INTRODUCTION

Nowadays, scientists try to find methods which conveniently assess the degree of fungal growth in food at a very early stage and well in advance to becoming visible to control food qualification [1]. Because the existence and growth of fungi may cause spoilage and result in a reduction in quality of foods [2]. It produces mycotoxins in foods, fruits, vegetables and feedstuffs causing important economic losses due to spoilage [2-4]. Mycotoxins are known to be effective hepatocarcinogens in animals and humans, a substance that causes cancer of the liver [2]. As living beings, the activation of fungi in food is accompanied by the production of some gaseous products such as CO_2. Thus, producing sensors for detection of these gases helps Detection of the start of food decay at early stages. These sensors should be safe and easily available [5]. It is expected that sensing methods with the help of nanotechnology will lead to the detection of the gases on a molecular scale due to surface enhancement. The electric resistance of a gas sensor at its working temperature changes considerably due to various chemical reactions happening between the sensor materials and the gases [6].

Tin oxide (SnO_2) and Tin disulfide (SnS_2) are known as materials used to a capacious kind of gas sensor for sensing and detecting a great number of gases due to their special optical and electrical properties [7-9]. SnO_2 and SnS_2 thin films have been synthesized by a variety of physical and chemical methods such as; chemical vapor deposition (CVD) [10], electrochemical deposition [11], chemical bath deposition [12], spray pyrolysis [13], electron beam-induced deposition [14], and vacuum evaporation [15]. Among these methods, spray pyrolysis has some advantages such as; cheap,

* Corresponding Author Email: *rahilradfar@yahoo.com*

facility of doing, and the possibility to coat large surfaces in mass production, comparing to the other methods [16].

In this paper, SnO_2 and SnS_2 nano films were deposited by spray pyrolysis method on glass surfaces. Structural properties of the prepared films were investigated by (XRD) and (SEM). The bio sensing properties of the samples were measured in the presence of the produced toxic gases from A. Niger fungi.

EXPERIMENTAL

Synthesis of the thin films

Stannic chloride ($SnCl_4.5H_2O$), ethanol (C_2H_5OH) and dimethyle thiourea (H_2NCSN_2H) were purchased from Merck Company, and were used as initiator materials without any further purification to synthesize SnO_2 and SnS_2 thin films. Both SnO_2 and SnS_2 thin films were synthesized on glass substrates using spray pyrolysis method. Before the deposition process, the glass substrates were washed ultrasonically and dried. In order to deposit SnO_2 thin film, a prepared solution of 33% wt $SnCl_4.5H_2O$, 33% wt H_2O, 33% wt C_2H_5OH and 1% wt HCl was sprayed, through a nozzle of 0.1 mm bore diameter and air as the carrier gas. The temperature of the substrate was kept at 500 ˚C during the deposition process. The conditions of spray pyrolysis were controlled by nozzle to substrate distance of 40 cm, carrier-gas pressure of 3 atm, spray deposition rate of 5 ml/min and hot plate rotation speed of 60 rpm. The prepared thin films were then cooled down to room temperature naturally.

On the other hand, to prepare tin disulphide films the temperature of the hot plate was fixed at 350°C. The precursor solution was prepared by dissolving 7 g Stannic chloride ($SnCl_4.5H_2O$), 4.5 g dimethyl thiourea (H_2NCSN_2H) in a solution of isopropyl alcohol and deionized water. The ratio of alcohol to water was chosen as 3:1. The deposition parameters such as solution flow rate, carrier-gas pressure, hot plate rotation speed and nozzle to substrate distance were kept constant at 10 (ml/min), 3 (atm), 60 (rpm) and 35 cm, respectively. Finally, the temperature of the prepared thin films decreased to room temperature naturally.

Preparation of the A.niger medium

Dehydrated potato dextrose agar was dissolved in water by stirring at 40 ˚C in order to obtain a cloudy yellow solution. The solution was cooled down to the room temperature and then poured into petri plates. The agar medium was inoculated by A. niger resulting in a substantial colony of fungus after 5 to 7 days.

Characterization

The crystalline structures of the synthesized thin films were characterized by a X-ray diffractometer (Bruker D8 Advance diffractometer Model, Ettlingen, Germany) with Cu-K_α radiation and wavelength of $\lambda = 1.5418$ Å. The surface morphology of the prepared thin films was analyzed using a scanning electron microscope (SEM model LEO 1450 VP System Oberkochen, Germany). Nano-biosensor test was done by measuring the resistance of the SnO_2 and SnS_2 thin films in the presence of the produced gases from the A. niger at different times and temperatures.

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD)

Fig. 1(a) displays the XRD pattern of SnO_2 thin film. Various peaks of the graph such as (110), (200) and (211) reveal that the sample has a crystalline

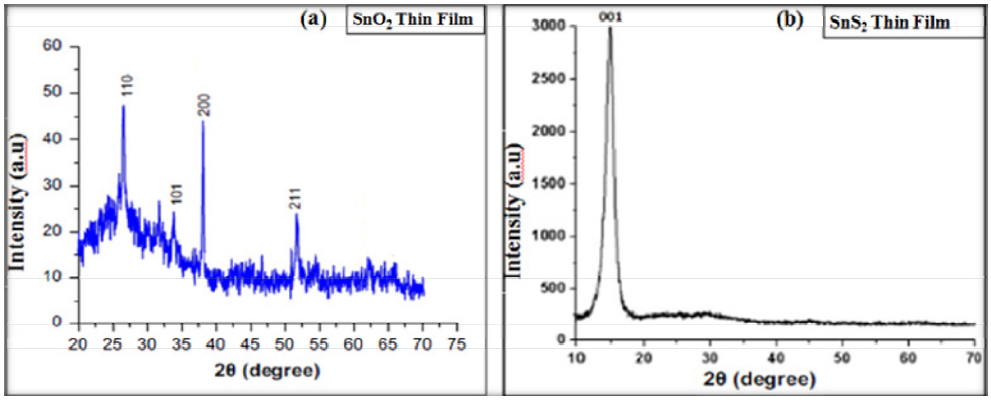

Fig. 1. XRD Pattern of a) SnO_2 and b) SnS_2 thin films

structure with tetragonal phase (PDF Card No: 00-005-046). The average crystallite size of the SnO_2 thin film was estimated to be about 17-23 nm using Scherrer's formula.

XRD figure of the SnS_2 thin film is presented in Fig. 1(b). It can be seen from the graph that the sample has polycrystalline structure with hexagonal phase (PDF Card No: 00-001-1010). The pattern indicates that the film is formed at this temperature with a strong peak (001) at about $2\theta = 15^o$, which refers to the growth of the sample in a single direction on the substrate. The average crystallite size is estimated to be about 8 nm calculated by Scherrer's formula for the SnS_2 thin film.

Scanning electron microscopy (SEM)

The SEM figures of the prepared thin films are given in Fig. 2(a and b) which show the formation of uniform thin films by nano-metric scale grains. The average sizes of SnO_2 and SnS_2 particles are about 62 nm and 87 nm, respectively**.** In addition, as regards the surface morphology, the SEM images depict that both SnS_2 and SnO_2 thin films possess high porosity and specific surface area making them a promising choice in sensors applications.

Nanobiosensor properties

Two separate closed vessels were chosen and SnO_2 and SnS_2 thin films were put into each of them. In each vessel, blank samples were also put for comparison. A. Niger fungi were cultured on the thin films and the blank media, and the vessels were considered as the study cases. To study the sensor-like behavior of the thin films, a designed system for calculating electrical parameters, such as current and voltage is needed. First, the resistivity of the samples, which were placed in both vessels, was measured versus time over 2 days. Then, silica-gel was used in both aforementioned media in order to reduce the humidity, and the measurements were

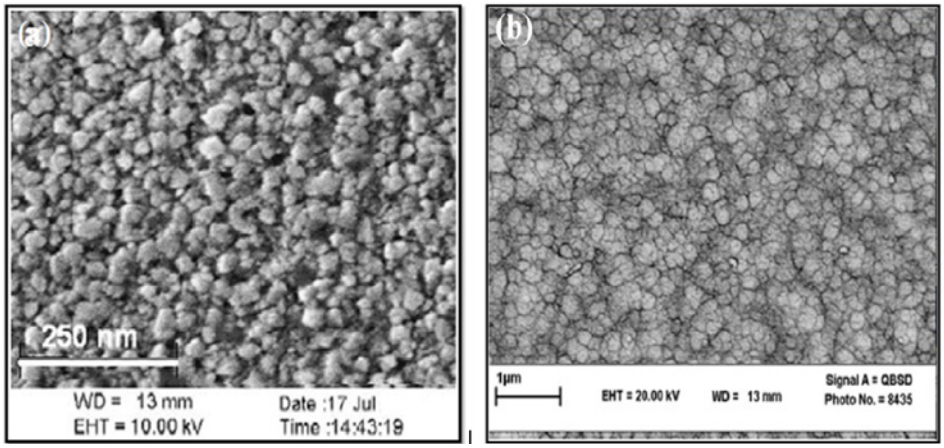

Fig. 2. SEM photographs of a) SnO_2 and b) SnS_2 thin films

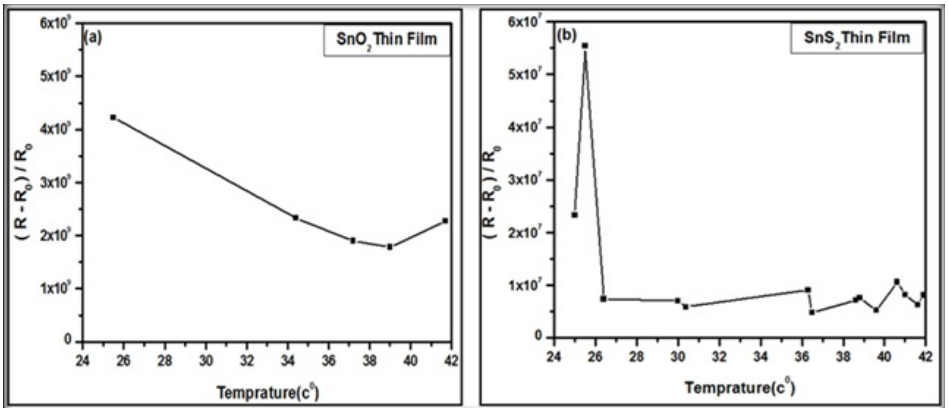

Fig. 3. plot variation resistance according to time for a) SnO_2 thin film and b) SnS_2 thin film

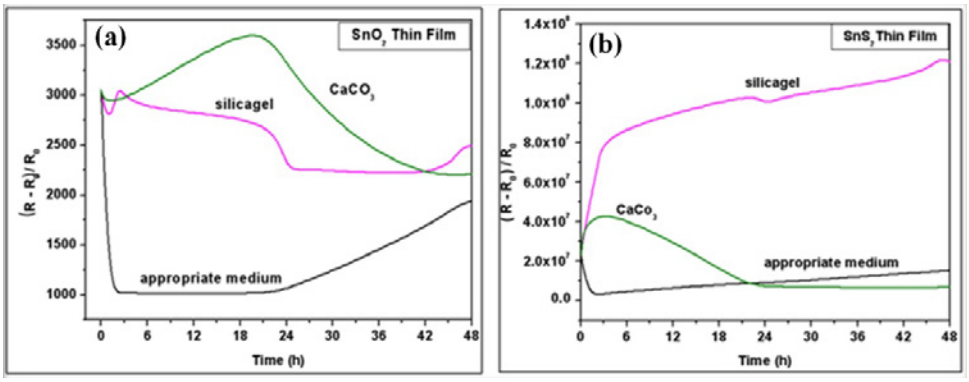

Fig 4. plot variation resistance according to temperature for a) SnO_2 thin film and b) SnS_2 thin film

repeated. Finally, the measurements were applied in the presence of $CaCO_3$. $CaCO_3$ was chosen to absorb the CO_2 of each medium.

The working mechanism of the sensors is explained in the following. The existing oxygen on the surface of a semiconductor is transformed to oxygen ion and leaves the surface. Then, the diffused gases from the mold react with these free oxygen ions. Therefore, the resistivity of the semiconductor changes due to the electron transportation during the occurred chemical reactions. The sensitivity of the thin films increases as the number of oxygen ions rises [17]. In addition, the sensitivity of the thin films increases with an increase in the temperature, yet it depends on the sensor type and diffused gases [18].

As can be seen, in Fig. 3 (a) the resistance of SnO_2 thin film decreases with time for one day, and after that starts to increase. Also, it is considered that the resistance of SnO_2 thin film exposed to silica gel increases dramatically in the primary hours, and then decreases time passes. In the primary hours, it is seen that the resistance of the sample in the presence of $CaCO_3$ increases significantly, and then decreases to a constant value.

Fig. 3 (b) displays that the resistance of SnS_2 thin film decreases with an increase in time, and after that it reaches a constant value. A remarkable increase in resistance is observed for the sample in presence of silica-gel comparing to the samples in the presence of $CaCO_3$. Also, the resistance of the sample decreases after one day in the presence of $CaCO_3$; whereas, the resistance continuously increases for the sample exposed to silica-gel. It has been reported before that the optimum temperature for growing A. Niger is about 37C˚ and the sensitivity of the sample depends on temperature [19]. Therefore, the temperature of the medium was controlled by an IR lamp and the resistivities of the samples were studied in respect to the temperature. Fig. 4 (a) displays that the resistance of SnO_2 thin film decreases as the temperature increases and reaches a minimum at 39˚ C, and then starts to increase at higher temperatures. On the other hand, the resistance of SnS_2 thin film increases at the beginning with a maximum at temperatures near 26˚ C, and then decreases, followed by negligible fluctuations, Fig. 4 (b).

CONCLUSIONS

SnO_2 and SnS_2 thin films were synthesized on glass substrates by spray pyrolysis method. The structure and morphology of the thin films were characterized by XRD and SEM techniques respectively. The crystallite sizes of SnO_2 and SnS_2 were obtained 17-23 nm and 8 nm, respectively. Also, the average grain sizes of the samples were obtained to be 62 nm and 87 nm for SnO_2 and SnS_2 samples, respectively. The biosensing properties of these thin films were investigated by measuring their electrical resistance in regular time intervals and at different temperatures and media in the presence of A. Niger fungi. The results revealed that both SnO_2 and SnS_2 samples are suitable candidates in fabrication of nanobiosensor, however, SnS_2 thin films show better sensitivity comparing to the SnO_2 thin films.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Azhir E. Etefagh R. Shahtahmasebi N. Mohammadi M. Amiri D. And Sarhaddi R. "Aspergillus Niger biosensor based on tin oxide (SnO2) nanostructures: nanopowder and thin film", J. Science and Technology. 5 (2012), 3010.
2. Irkin R. And Korukluoglu M. "Control of Aspergillus niger with garlic, onion and leek extracts", J. of Biotechnology. 6 (2007), 384.
3. Samson RA, Varga J. What is a species inAspergillus? Medical Mycology. 2009;47(s1):S13-S20.
4. Abdel-Hafez SII, Shoreit AAM. Mycotoxins producing fungi and mycoflora of air-dust from Taif, Saudi Arabia. Mycopathologia. 1985;92(2):65-71.
5. Carrascosa LG, Moreno M, Álvarez M, Lechuga LM. Nanomechanical biosensors: a new sensing tool. TrAC Trends in Analytical Chemistry. 2006;25(3):196-206.
6. Kim K-S, Baek W-H, Kim J-M, Yoon T-S, Lee HH, Kang CJ, et al. A Nanopore Structured High Performance Toluene Gas Sensor Made by Nanoimprinting Method. Sensors. 2010;10(1):765-74.
7. Yagi I, Hagiwara Y, Murakami K, Kaneko S. Growth of highly oriented SnO2 thin films on glass substrate from tetra-n-butyltin by the spray pyrolysis technique. Journal of Materials Research. 1993;8(07):1481-3.
8. Schierbaum KD, Weimar U, Göpel W. Multicomponent gas analysis: An analytical chemistry approach applied to modified SnO2 sensors. Sensors and Actuators B: Chemical. 1990;2(1):71-8.
9. Jiang T, Ozin GA, Verma A, Bedard RL. Adsorption and sensing properties of microporous layered tin sulfide materials. Journal of Materials Chemistry. 1998;8(7):1649-56.
10. Manasevit H.M. and Simpson W.J." Paper presented at Electrochemical Society Meeting ", J. Electrochem. 122 (1975), 444.
11. Takeuchi K, Ichimura M, Arai E, Yamazaki Y. SnS thin films fabricated by pulsed and normal electrochemical deposition. Solar Energy Materials and Solar Cells. 2003;75(3-4):427-32.
12. Engelken RD, McCloud HE, Lee C, Slayton M, Ghoreishi H. ChemInform Abstract: Low Temperature Chemical Precipitation and Vapor Deposition of SnxS Thin Films. ChemInform. 1988;19(9).
13. Arunyanart M, Love LJC. Model for micellar effects on liquid chromatography capacity factors and for determination of micelle-solute equilibrium constants. Analytical Chemistry. 1984;56(9):1557-61.
14. Fadavieslam M.R. Shahtahmasebi N. Rezaee-Roknabadi M. And Bagheri-Mohagheghi M.M." Reliability test and failure analysis of high power LED packages" J. Semiconductors. 32 (2011), 3002.
15. Koteeswara Reddy N, Ramakrishna Reddy KT. Preparation and characterisation of sprayed tin sulphide films grown at different precursor concentrations. Materials Chemistry and Physics. 2007;102(1):13-8.
16. Burton LA, Colombara D, Abellon RD, Grozema FC, Peter LM, Savenije TJ, et al. ChemInform Abstract: Synthesis, Characterization, and Electronic Structure of Single-Crystal SnS, Sn2S3, and SnS2. ChemInform. 2014;45(10):no-no.
17. Yamazoe N. New approaches for improving semiconductor gas sensors. Sensors and Actuators B: Chemical. 1991;5(1-4):7-19.
18. Bahrami B, Khodadadi A, Kazemeini M, Mortazavi Y. Enhanced CO sensitivity and selectivity of gold nanoparticles-doped SnO2 sensor in presence of propane and methane. Sensors and Actuators B: Chemical. 2008;133(1):352-6.
19. Szewczyk KW, Myszka L. The effect of temperature on the growth of A. niger in solid state fermentation. Bioprocess Engineering. 1994;10(3):123-6.