Indian Journal of Science and Technology Vol. 5 No. 7 (July 2012) ISSN: 0974- 6846

Aspergillus niger biosensor based on tin oxide (SnO_2) nanostructures: nanopowder and thin film

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Abstract

In this paper, SnO_2 thin film and nanopowder were prepared by spray pyrolysis and sol-gel methods, respectively. The SnO_2 nanostructures were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Then *Aspergillus niger* fungus were cultured in an appropriate medium and were exposed to the SnO_2 nanofilm and nanopowder. The nano-system electric resistance was measured in the presence of produced gases and the effect of time and temperature on nanobiosensors was studied. Then, SnO_2 nanobiosensor was characterized in the presence of silicagel and calcium carbonate.

Keywords: Nanobiosensor, *Aspergillus niger* fungi, Spray pyrolysis technique, Sol gel method.

Introduction

Nowadays, scientists are in search for newer measure to attain better food quality. *Aspergillus niger* is an important species used as production organisms in industrial fermentation for producing various substances. The safety of *A. niger* as production organism for food-high grade product has long been emphasized. For an example, the general use in food of *A. niger* derived citric acid has been affirmed as GRAS by the FDA in 1994 (Blumenthal, 2004).

Metal oxide SnO_2 is an attractive material for solar cells (Snaith & Ducati, 2010), gas-sensing and biosensor (Patil *et al.*, 2011) due to its high optical transparency and electrical conductivity. SnO_2 has a rutile tetragonal structure (Bagheri-Mohagheghi *et al.*, 2008). Some of the tin organic compounds have several applications as fungicides and insecticides for the agriculture and still as wood, textile and paper preservers.

The resistance of a gas sensor at the sensing temperature can be dramatically impressed by exposure to various chemical species (Kim *et al.*, 2010). Fluctuations in resistance are expected to be seen in most of the conducting media. There is a need to have devices for detecting food decay. These devices should be safe and easily accessible (Carrascosa *et al.*, 2006). Unfortunately, most of the resistive gas sensors work in temperatures higher than room temperature (Duran *et al.*, 2005).

In this paper, thin film of SnO_2 deposited by spray pyrolysis and its nanopowder synthesized by sol-gel technique. XRD, SEM and TEM investigated structural and micro-structural properties and in order to detect resulted toxic gas from the *A. niger*, the physical and electronic properties of SnO_2 were analyzed.

Experimental details

Synthesis methods

The SnO_2 thin film has been deposited on the glass substrates using a typical spray pyrolysis at substrate temperature of 500 °C. A precursor solution was prepared by using of 33% wt. $SnCl_4.5H_2O$, 33% wt. H_2O and 33% wt. C_2H_5OH solution. Nanopowder of SnO_2 was prepared by sol-gel method. For this purpose, a precursor solution was prepared by using ethanol (C_2H_5OH, Merck, >99.9%) and deionized (DI) Water as solvent (1:1) followed by addition of $SnCl_4.5H_2O$. Then citric acid and ethylene glycol were used as polymerization and complexion agents, respectively. Finally, the powder was annealed at 500 °C for 1 h in oven.

Characterization details

The samples were characterized by using XRD (D8 Advance Bruker). The average crystallite size of powders was estimated using the Scherrer's formula (Scherrer, 1918). SEM using LEO 1450 VP System studied the surface morphology of film. TEM (LEO 912AB) was also used for estimation of crystalline structure, morphology and mean size of nanopowder. Nanopowder was formed into tablet. The tablet was placed between two glass slides in which a hole was punched out in the middle of each slide by the diameter less than tablet one. The tablet was attached to the slides using silver glue. A system consisting of SnO_2 thin film and SnO_2 tablet prepared in two distinct desiccators was devised to study the sensor-like behavior. Here, one of the two acted as a control, the other was regarded as a target, and each one was put in the exposure to *Aspergillus niger* cultured in appropriate media. Then, resistant of the layers was measured in the presence of silica gel (to absorb moisture) and calcium carbonate (to omit carbon monoxide), using the designed system composed of a voltage source and a nano amper meter for 48 hours. Nanobiosensor test was done by measuring the resulting resistance of the nano film and tablet of SnO_2 in different times.

Results and discussion

Structural properties

Fig 1(a-b) shows the XRD pattern of SnO_2 nano film and nanopowder. As seen, all samples have crystalline

Indian Journal of Science and Technology Vol. 5 No. 6 (June 2012) ISSN: 0974- 6846

Fig. 1. XRD Patterns of SnO_2 for (a) Thin film (b) Nanopowder

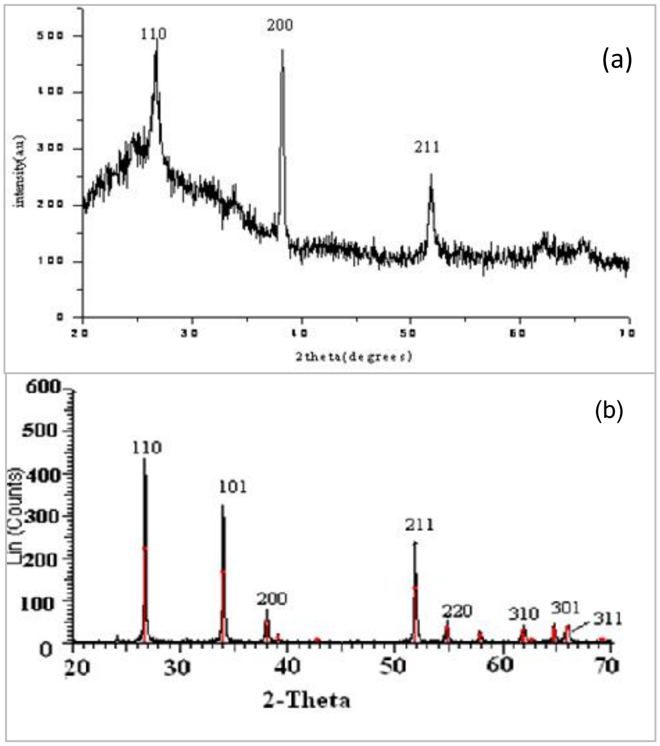


Fig 2. SEM photograph of SnO_2 thin film

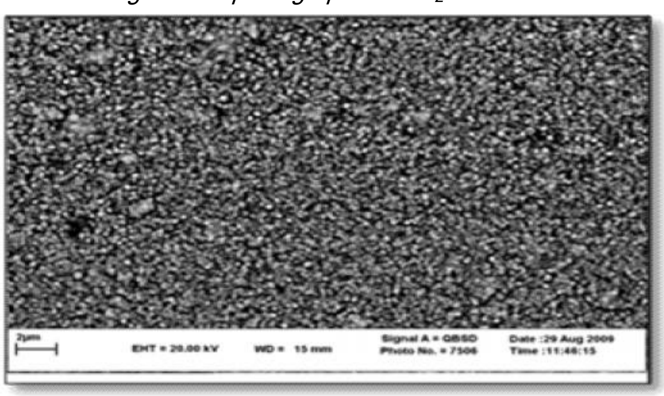


Fig 3. TEM image of SnO_2 nanopowder

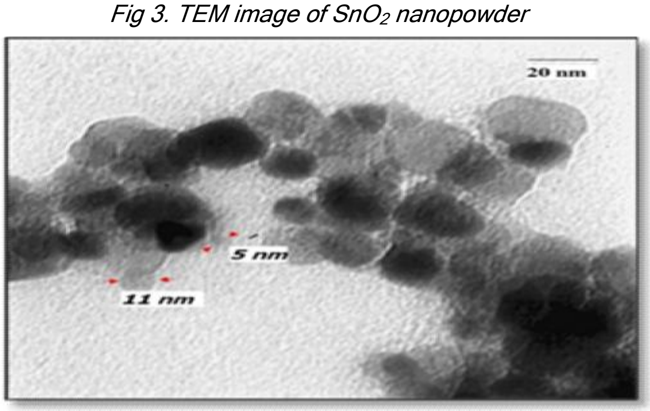


Fig 4. A device for measuring sensor-like behavior

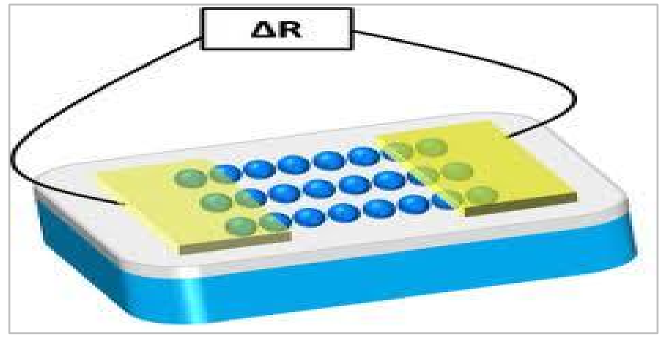
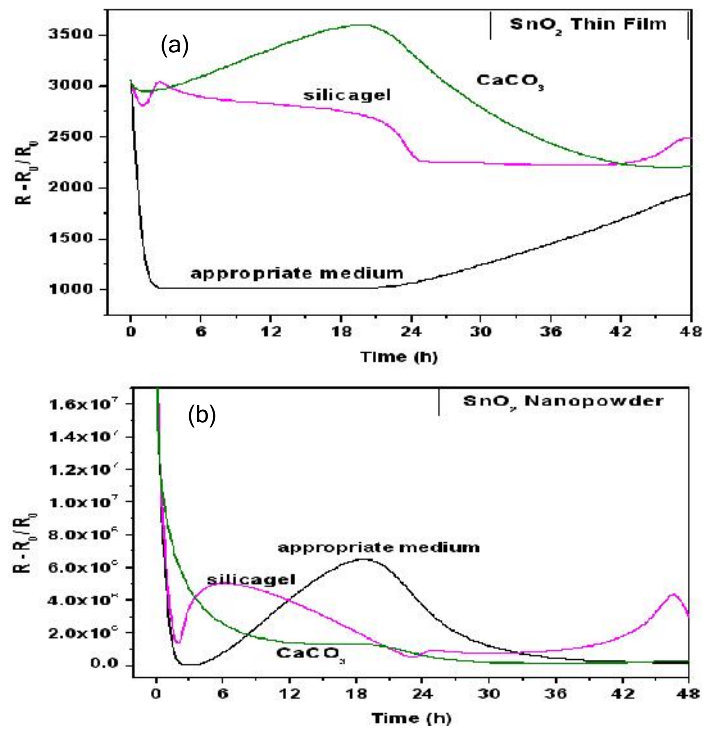


Fig. 5. Plot variation resistance according to time for SnO_2 (a) Thin film and (b) Nanopowder



structure with rutile tetragonal structure. The average crystallite size of nano particles of SnO_2 estimated about 17-23 nm for the films and 8-17 nm for the nanopowder (by Scherrer's formula).

The SEM image of the film has been shown in Fig 2 which confirms the existence of particles in nanometric scale. It has been observed that film has uniform topology with particle diameters bigger than the ones estimated by Scherrer's formula calculated from XRD pattern.

Fig. 3 shows a typical TEM micrograph of SnO_2 nanopowder. An agglomeration of nanoscale particles is clearly observed, showing a uniform distribution of particle size and a homogeneous morphology. Particle-size distribution histogram of SnO_2 nanopowder indicated that average diameter of nanopowder calculated from TEM image are about 5-25 nm.

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Biosensor properties

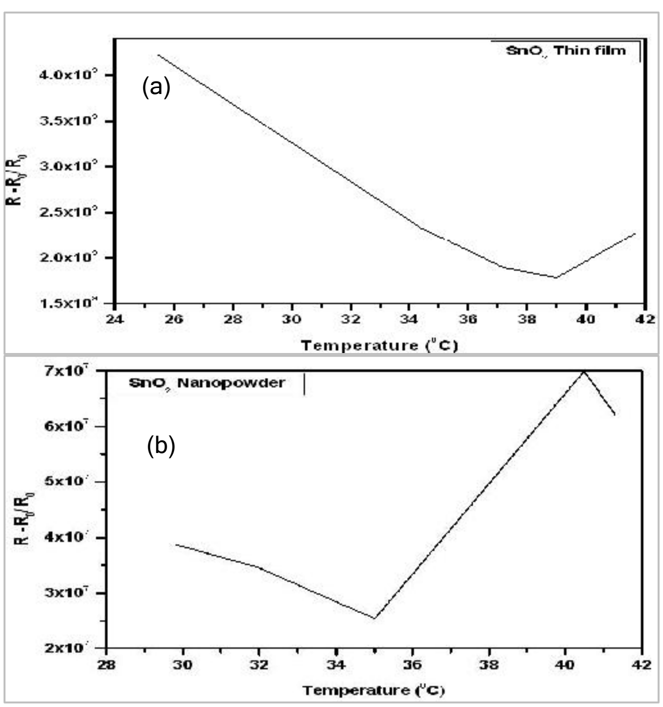
A device for calculating electrical parameters such as current and voltage is needed to study the sensor-like behavior of nano film and tablet of SnO_2. Such device is shown in Fig. 4.

The optimum temperature for nanometric film and tin oxide Nano powders is about 37 ^oC. The suitable heat in this work was provided by an IR lamp. The resistance of samples has been measured with a nano ampere meter against time during 2 days. Silica gel in the second step was used in the both mentioned medium in order to reduce the humidity of the medium. The $CaCO_3$ was also applied for absorbance of CO_2 of the medium in third experiment. Variation of resistance versus time and temperature have been shown in Fig 5 (a-b) and Fig 6 (a-b), respectively.

As the temperature increases, the resistance of SnO_2 thin film diminishes at first but shows subsequent increase in temperatures of 39 ^oC and above. On the other hand, the resistance of SnO_2 tablets decreases at first as the temperature nears 35 ^oC, followed by a subsequent increase. Another decrease in resistance is observed in temperatures of 40 ^oC and above.

When atmospheric oxygen is absorbed on the surface of a semiconductor, it is transformed to oxygen Ions. This chemical absorption causes the formation of a charge-space (barrier layer) zone on the surface of that semiconductor. Then, the disseminated gases from the mold will react with the oxygen Ions in the surfaces. The faster this reaction is; more electrons will be donated to the semiconductor and the quicker the empty layer will be downsized (which consequently leads to increased

Fig 6. Plot variation resistance according to temperature for SnO_2 (a) Thin film and (b) Nanopowder



sensitivity of the sensor). Sensor sensitivity increases as temperature rises; but this is not an everlasting trend and this parameter saturates at a certain temperature which depends on the gas and the sensor type. From that point on, further increase in the temperature will reduce the sensitivity. This is because in significantly higher temperatures, the product of the gas-oxygen reaction present at the sensor surface tends to escape form the solid surface; something which is not seen in lower temperatures.

Conclusions

Crystalline thin film of SnO_2 has been deposited on glass substrates by the spray pyrolysis and nanopowder synthesis by sol-gel technique. Structure and morphology of thin film and nanopowder of SnO_2 were characterized by XRD, SEM and TEM respectively. The SnO_2 nanobiosensor in the presence *A. niger* fungi is responded quickly with change of electrical resistant. It has been seen a decreasing in resistance by adding silica gel in tin oxide.

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