Ethylene glycol Sensing Properties of Tin Dioxide (SnO_2) Thick Films: A Promising EG Sensor for Environmental Monitoring

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***Abstract*: -**

This study explores the Ethylene glycol (EG) sensing capabilities of Tin Dioxide (SnO_2) thick films, presenting a novel approach for developing an EG sensor tailored for environmental monitoring. SnO_2 thick film deposition by screen printing method, the SnO_2 thick films underwent comprehensive characterization employing X-ray diffraction (XRD) for structural analysis, Fourier-transform infrared spectroscopy (FTIR) for chemical identification, scanning electron microscopy (SEM) for morphological examination, and thermo gravimetric-differential thermal analysis (TG-DTA) for thermal stability assessment. XRD confirmed the tetragonal rutile structure of the SnO_2 thick films, ensuring their crystalline nature. FTIR spectra verified the purity of the material, and SEM images depicted a uniform surface morphology crucial for optimal gas sensing. TG-DTA provided insights into thermal stability. Subsequently, integrated into an EG sensor platform, the SnO_2 thick films demonstrated excellent gas sensing characteristics. Operating temperature optimization ensured efficient performance, and the sensor exhibited rapid response and recovery times, reaching saturation promptly. Moreover, the EG sensor demonstrated remarkable stability under diverse gas concentrations, showcasing its potential as an efficient and reliable tool for real-time environmental monitoring. This research establishes SnO_2 thick films as a promising candidate for addressing contemporary environmental challenges through EG sensing capabilities.

Keywords: Tin oxide, XRD, FTIR, SEM, TG-DTA and an EG sensor.

1. Introduction

Environmental air pollution, caused by natural processes or human activities, poses risks such as respiratory issues, cardiovascular effects, and climate change [1]. Detection of hazardous gases, including ethylene glycol commonly used in various industries, is crucial for human health and environmental protection. Ethylene glycol, found in antifreeze, deicing agents, and manufacturing, poses health risks if ingested, can contaminate soil and water, and harms aquatic life [2-5]. Proper handling and disposal procedures, along with adherence to regulatory guidelines, are essential to minimize risks. With effective detection and mitigation strategies, the impact of EG on human health and the environment can be reduced [6].

Tin dioxide (SnO_2) is extensively used in gas sensing due to its semiconducting properties and high sensitivity. Applications include environmental monitoring (air quality, pollutants), industrial safety (hazardous gases), automotive (exhaust gases, fuel efficiency), home safety (gas leaks), medical devices (patient health monitoring), food industry (freshness control), fire detection, oil and gas exploration (safety monitoring), emission control (pollutant monitoring), and electronic nose devices for various applications like odor detection and quality control [7, 8]. As the classical gas sensing material, SnO2 has been widely used in gas sensors due to its low cost, higher chemical sensitivity, faster gas response and good stability. In general, SnO2 displays excellent gas detection properties for volatile organic compound vapors and toxic gases, such as acetone [9, 10], ethanol [11], hydrogen [12], formaldehyde [13] , etc. However, some problems still need to be solved for the SnO2 gas sensor, such as low selectivity, slow response or recovery rate and poor response.

In this context, our study focuses on harnessing the gas sensing potential of SnO_2 through the development of EG sensors, specifically employing SnO_2 thick films. These thick films offer a versatile platform for gas sensing applications. Their unique structural and chemical properties make SnO_2 an ideal semiconductor for detecting a wide range of environmental pollutants.

2. Experimental

2.1. Material Preparation

SnO_2 and ethylene glycol were provided by Sigma Aldrich and S.D. Fine Chemical Limited (SDFCL) for the experimental study, and no additional purification was conducted. Comprehensive characterization of SnO_2 is essential, necessitating the utilization of various analytical methods to unveil details about its structural, functional, thermal, and morphological characteristics.

XRD patterns were obtained using CuKa radiation (λ= 1.543 Å) and a Rigaku diffractometer (Miniflex) in the 2θ range of 20° to 60° for crystalline structure determination. Shimadzu FTIR spectrophotometer identified functional groups through a 40-time scan at 4 cm^{-1} resolution (4000 to 400 cm^{-1}). Thermal behavior in an air-filled environment was studied using a Shimadzu Thermal Analyzer, with samples subjected to a temperature rise from 28°C to 800°C at 10 °C/min. JSM6360 scanning electron microscopy analyzed surface morphology and chemical content.

2.2. Thick film preparation

For SnO_2 thick film preparation, mix SnO_2 powder, binder, and solvent to create a homogeneous paste with a component ratio based on desired viscosity and film properties. Adjust paste viscosity with BCA solvent. Squeeze the paste through a porous mesh onto a pre-cleaned glass substrate, forming a 1x2 cm2 film. Dry the screen-printed films for 24 hours to remove temporary binders. Anneal the films in air at 550°C for 2 hours in a programmable furnace for noble deposition of functional material on the glass substrate [14].

2.3. Gas sensing performance

Our laboratory has designed, fabricated, and standardized an immobile gas sensor device. This custom-built apparatus is dedicated to studying the gas sensing characteristics of SnO_2 thick films.

To mitigate the impact of relative humidity, experimentation is conducted using preheated samples ranging from room temperature to 300 °C. The sensor's resistance undergoes changes in the presence of air and gas, with the Gas response S (%) calculated using the formula: [15].

$$Gas\ response\ S(\%) = \frac{R_g - R_a}{R_a} \times 100 \quad (1)$$

Where R_a and R_g stand for the sensor's resistance in air and gas, respectively.
Several key factors, including operating temperature, response/recovery time, gas absorption ability, repeatability, and stability, are considered to evaluate the sensor's performance.

3. Result and Discussion

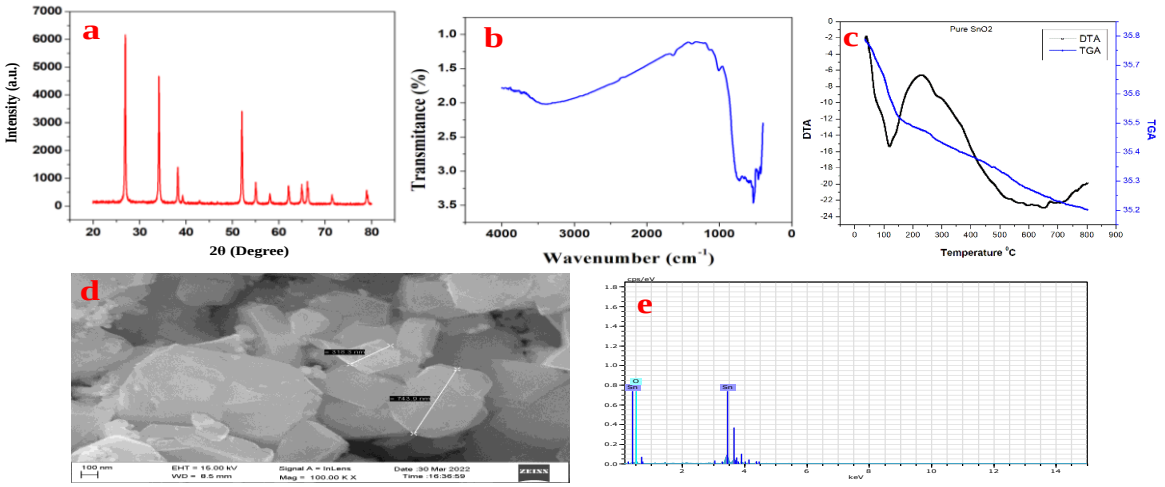

Fig.1. (a) XRD Spectra (b) FTIR Spectra (c) TG-DTA (d) SEM and (e) EDAX of SnO_2

Fig.1.(a) indicate the X-ray spectra of SnO_2 powder. The XRD pattern of the product reveals peaks corresponding to (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0), and (3 0 1) planes, confirming a tetragonal SnO2 structure. This aligns with JCPDS card no. 41–1445. The average particle size, estimated at 22.4 nm using the Scherrer equation, signifies the crystallite size based on XRD analysis [16, 17].

The FT-IR spectrum of SnO_2 nanoparticles Fig.1.(b) was recorded using shimadzu FTIR spectrometer in the 400–4000 cm–1 wavelength range via the KBr pellet technique. The FT-IR spectrum of microwave-treated SnO_2 nanoparticles exhibited distinct changes. Initially, a terminal oxygen vibration (νSn–OH) band at 539 cm−1 was observed in the dried precipitate. Microwave treatment resulted in the transformation of hydroxyl groups into oxide groups, eliminating the νSn–OH band. Subsequent heating at a higher temperature (1KW) induced the appearance of a new broad band at 620 cm−1, characteristic of oxide-bridge functional groups (νOSnO), indicating a transition from SnO_2 to SnO. Peaks at 1631 cm−1 suggested NH vibrations, possibly related to ammonia. The absorption band at 3323 cm−1 was attributed to νOH stretching vibrations of surface hydroxyl groups or adsorbed water. Even at low pH, some residual OH groups persisted, likely due to re-absorption of water from the ambient atmosphere.

This FT-IR analysis provided insights into the structural changes and functional groups during the microwave treatment and subsequent sintering process [17]. Fig.1.(c) shows the TG–DTA pattern of the SnO_2 powder. In this figure, a deep and sharp endothermic peak is obtained at 96°C with weight loss of 24 % in TG curve. The endothermic effects may be corresponding to the oxidation and decomposition of organic materials. In addition, weight loss is attributing to evaporation of physical absorbed water from the surface of sample [16, 17]. The weight loss of 92 % is continued until about 400°C. It is probably due to complete decomposition of SnO_22H_2O and the formation of SnO_2 nanoparticles. Although beyond 400°C no weight loss is observed, thus, 400°C is chosen as an appropriate calcination temperature to obtain pure SnO_2 [16, 17]. SEM analysis of SnO_2 nanoparticles Fig.1.(d) revealed a typical morphology with particles averaging about 1 µm or less. The SnO_2 nanoparticles exhibited a distinct spherical shape in this study [16, 17]. The EDX spectrum in Fig.1.(e) confirms the presence of elemental tin, oxygen, and stannum oxide in the synthesized SnO_2 nanoparticles. No other elements were detected, indicating high purity [16, 17].

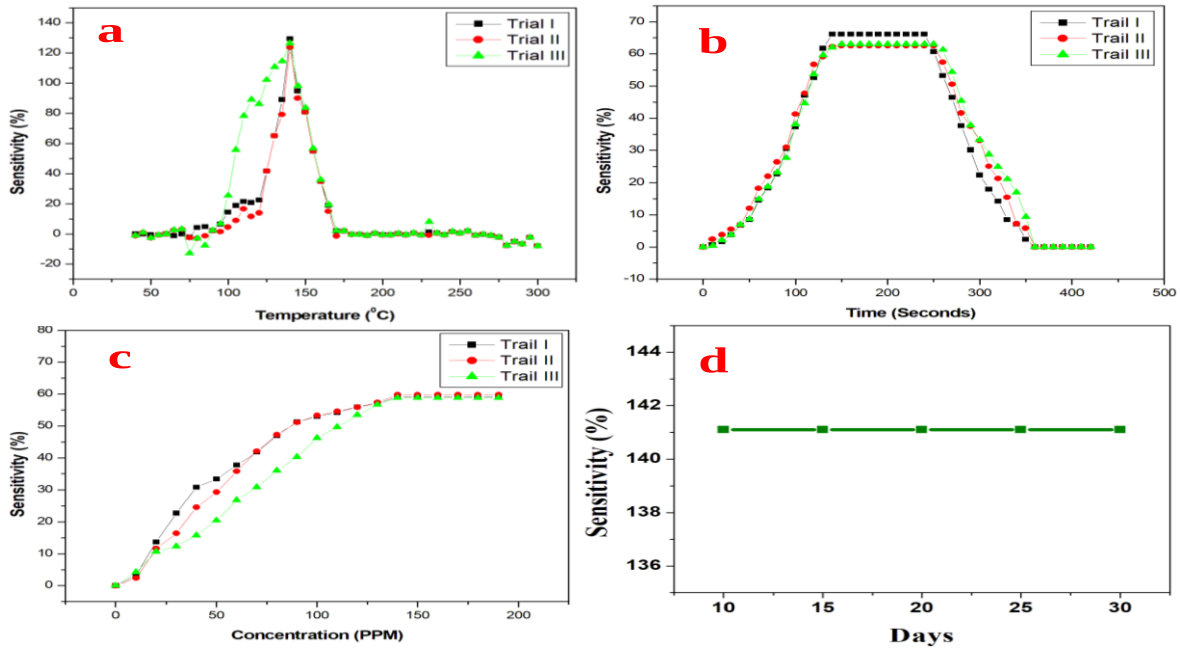

Fig.2. Sensing characteristics as (a) Operating Temperature (b) Response and Recovery time (c) Gas uptake capacity and (d) Stability of SnO_2 thick films

Fig.2. (a) displays a new SnO_2 thick film sensor responding to ethylene glycol at 140°C with a sensitivity of 137%. The sensor demonstrates inherent sensitivity to ethylene glycol, particularly effective at 140°C, indicating lower operating temperatures compared to alternative sensors. Response and recovery times of the SnO_2 sensor are influenced by the concentration of ethylene glycol vapors. Higher concentrations lead to faster responses, but saturation effects may impede recovery. Despite low exposure (2 ppm EG), the sensor unit shows rapid recovery. In Fig.2. (b), SnO_2 detects EG vapors within 120 seconds of exposure to (air+EG) and recovers within the same timeframe when exposed to air again. In Fig.2. (c), the saturation limit of a tin oxide (SnO_2) ethylene glycol vapor sensor is shown.

This limit signifies the concentration at which the sensor's response plateaus, indicating saturation where all sensing sites on the SnO_2 surface are occupied by the target gas molecules, resulting in a constant sensor response. Fig.2. (d) reveals sustained stability of the ethylene glycol (EG) sensor, with readings taken every five days at a fixed 2 ppm EG concentration. It confirms reproducibility by exposing sensors to consistent EG concentrations over 30 days (5 cycles), showing consistent performance.

4. Conclusion

This study investigates the potential use of Tin Dioxide (SnO2) thick films as sensors for detecting ethylene glycol (EG) in environmental monitoring applications. The research explores various aspects of the SnO2 films, including their structural properties, morphology, sensitivity, response time, saturation effects, and stability over time. Firstly, the structural characteristics of the SnO2 films are examined using X-ray diffraction (XRD). The results reveal a tetragonal rutile structure, indicating the crystalline nature of the films. This structural confirmation provides insight into the stability and phase composition of the SnO2 material, which is crucial for its sensor performance. Next, the purity and uniformity of the SnO2 films are evaluated using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). FTIR analysis helps in identifying functional groups and confirming the absence of impurities in the films. SEM imaging provides detailed information about the surface morphology, ensuring that the films are uniform and free from defects, which is essential for reliable sensor operation. The SnO2 thick films are then integrated into EG sensors, and their performance characteristics are assessed. The sensors are operated at an optimal temperature of 140°C, where they exhibit maximum sensitivity towards EG. The sensitivity of the SnO2 thick films is reported to be 137%, indicating their ability to detect EG at low concentrations. Furthermore, the response and recovery times of the EG sensor are investigated. The results show that the SnO2 thick films exhibit rapid response and recovery times, even when exposed to low concentrations of EG (2 ppm). This suggests that the sensor is capable of quickly detecting changes in EG concentration in the environment. Saturation effects are also observed in the EG sensor, indicating a concentration plateau beyond which the sensor's response does not increase significantly. Understanding saturation effects is crucial for determining the dynamic range and limits of detection of the sensor. Finally, the long-term stability of the EG sensor is evaluated over a period of 30 days. The results demonstrate sustained stability, indicating that the SnO2 thick films maintain their sensing performance over time. This highlights the potential of SnO2 thick films as promising materials for efficient and reproducible EG sensing in environmental monitoring applications.

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