igMin Research STEM ISSN: 2995-8067 A Multidisciplinary Open Access Journal

TECHNOLOGY SUBJECT
Materials Science | Materials Engineering | Sensor | Applied Engineering TOPIC(S)

Article Information

Submitted: January 09, 2024
Approved: February 09, 2024
Published: February 12, 2024

How to cite this article: Nagar R, Kamathe V. Efficient Room Temperature Ethanol Vapor Sensing by Unique Fractal Features of Tin Oxide. IgMin Res. Feb 12, 2024; 2(2): 097-0101. IgMin ID: igmin150; DOI: 10.61927/igmin150; Available at: www.igminresearch.com/articles/pdf/igmin150.pdf

Keywords: Tin oxide; Fractals; Dendrites; Ethanol sensing; Ambient conditions

Research Article

Efficient Room Temperature Ethanol Vapor Sensing by Unique Fractal Features of Tin Oxide

Rupali Nagar* and Vishal Kamathe

Nanomaterials for Energy Applications Lab, Applied Science Department, Symbiosis Institute of Technology, Symbiosis International (Deemed University), Lavale, Pune-412115, Maharashtra, India

***Correspondence:** Rupali Nagar, Nanomaterials for Energy Applications Lab, Applied Science Department, Symbiosis Institute of Technology, Symbiosis International (Deemed University), Lavale, Pune-412115, Maharashtra, India, Email: rupali.nagar@sitpune.edu.in

Abstract

Fractals are complex structures that repeat themselves at several scales. Nature exhibits these in many forms like snowflakes, mountains, coastlines, the human brain/lungs/ nervous system, and many more. It appears that these are nature's organic way of growth. Thus, there is an underlying science that works to grow or create these self-similar patterns. In this work, tin oxide-based fractals have been grown under laboratory conditions and applied to a gas-sensing field. The facile growth methodology successfully grows fractals on a large scale. The tin oxide fractals have unique basic building units that connect and grow in different directions. These tin oxide fractals have successfully sensed ethanol vapors in the range of 20 ppm to 100 ppm. The best sensing response has also detected ethanol vapors as low as 10 ppm at room temperature with response and recovery times of 18 ± 3 s and 22 ± 5 s, respectively. The best sensing response recorded for such sensors was under 12 s. The characteristic fractal growth is attributed as the defining factor that enhances ethanol sensing at room temperature.

Introduction

As digital technologies become more widespread research on sensors and device communication in the automation field needs to be given due attention. Highly sensitive sensors that can adapt to different environmental conditions are necessary for effective device interaction. In order to progress in the digital age, sensors and device communication systems must work together. Figure 1 depicts the US sensor market's over-year growth in demand for sensors that can detect different gases [1]. Ethanol sensors are used in various industries like chemical, food, ethanol production, and breweries [2-4]. It is critical to have an efficient sensor capable of operating at room temperature, as sensors operating at higher temperatures consume more power. Many metal oxides, including Sn, Zn, Ti, and others, have found application as sensors [5-9]. However, easy synthesis methodology along with good sensing behavior is always not easy to address. Researchers frequently use techniques like doping, annealing, dispersing nanoparticles, etc. to improve sensor performance [10-13]. Morphology is one of the crucial factors in semiconductor oxide gas sensor study since it provides a platform for the adsorption of gas analytes and deciding the rate of reaction to take place on the sensing surface. Sensing surfaces with significant morphology greatly improves gas-sensing abilities [14,15].

In this work tin oxide fractals with various morphologies were obtained by the sol-gel assisted method followed by the microwave irradiation technique. The precipitate thus obtained was dried under a hot air oven. The dried sample showed fascinating fractal morphologies at macro scales with branching structures. The prepared fractal morphology exhibited efficient ethanol vapor sensing detection ability without applying any heat treatment to the prepared sensor.

Materials and methods

To obtain the fractal-like morphologies, chemicals such as tin chloride pentahydrate ($SnCl_4.5H_2O$, 98% purity) and Urea (H_2NCONH_2, 99% purity) were received from Molychem (India) and Fisher Scientific (India), respectively and used further without any purification. Deionized water was used throughout for synthesis purposes. Briefly, sols were prepared in aqueous media using tin chloride pentahydrate and urea, the details can be found elsewhere [16]. No heating was applied at any stage. The reaction mixture was irradiated by microwaves at 595 watts. The reaction mixture turned turbid after 8 minutes and was allowed to cool naturally. Thereafter, it was dried in a hot air oven at a moderate temperature of 70 °C until completely dry. When fractals of different sizes and shapes emerge. The white precipitate formed was crushed manually using an agate mortar and pestle and stored in clean and dry conditions under a vacuum until further use.

X-ray diffraction (XRD) was used to examine the sample's phase formation and crystalline structure by using a Rigaku, Miniflex-600 instrument with Cu-Kα radiation at a wavelength of 1.5418 Å. The functional groups present in the sample were investigated using Shimadzu IR Affinity 1 FTIR spectroscopy. A gas-sensing apparatus by Prism Electronics Systems, India with 5V dc bias voltage was used for investigating the gas-sensing characteristics of the samples at room temperature. The response of the sensor was measured by changing the electrical resistance of the sensor with respect to the specific concentration of ethanol vapor exposed to the sensor at room temperature.

Results and discussions

In this work, fractal morphology forms as a result of precisely calibrated heating and salt concentration. The sol-gel-assisted method, followed by microwave irradiation, provides an easy and inexpensive method to synthesize the material. The fractal morphology was reported for other oxide materials by various synthesis techniques such as chemical vapor deposition, hydrothermal, sol-gel, microwave, pulse vapor deposition spray pyrolysis, etc [17-22]. In order to form fractal morphologies of various materials, it is difficult to optimize temperature and synthesis parameters. Furthermore, accurately determining the fractal characteristics of various morphological fractal structures is sometimes difficult. The fractal morphology of the tin oxide material obtained in this work is simple and at a lower temperature when compared to other published work. Figure 2(a,b) shows the tin oxide fractals grown on a glass substrate with very fine dendritic structures. The XRD analysis revealed the presence of impurities in the as-synthesized sample. Whereas, diffraction peaks at 26.6°, 33.8°, 37.8°, 51.6°, 54.2°, 57.8°, 62, 65°, 71.3° and 78.7° corresponded to the (110), (101), (200), (211), (220), (002), (310), (112), (202) and (321) crystal faces of tetragonal SnO_2 structure respectively for annealed sample at 400 °C. All the diffraction peaks match well with JCPDS card number 041-1445 of SnO_2 [23,24]. There were no impurities and characteristic peaks of other types of tin oxide found. Figure 2(c) shows that the X-ray diffractogram collected on the sample annealed at 400 °C in air and inset with the X-ray diffractogram of the as-synthesized fractal sample. The crystallite size of the as-synthesized and annealed sample was calculated to be 45 ± 5 nm and 10 ± 2 nm respectively by using Scherrer's equation [25]. Whereas, according to the Williamson-Hall (W-H) model size and strain broadening have been obtained by considering peak width as a function of 2θ [26,27]. The W-H model resulted in a crystallite size of maximum intense peak of the annealed sample to be 9.2 nm and a strain value be 0.2%.

The FTIR spectrum shown in Figure 2(d) was analyzed to identify the structural information of functional groups present on the surface of the sample. The absorption peaks at 535 cm^{-1} and 866 cm^{-1} indicate O-Sn-O and Sn-OH stretching vibration mode, respectively. The peaks at 1465 cm^{-1} are attributed to stretching vibrations of the O-H bond [28,29]. Weak peaks detected around 2300 cm^{-1} are most likely due to water or CO_2 being absorbed from the surrounding atmosphere.

Numerous studies have looked into the performance of fractal-based gas sensors. Some studies concentrate on the fractal morphologies of sensing materials at different temperatures, while others look into the fractal-shaped structure of the sensing substrate with varying dimensions [30-33]. The ultimate goal of this investigation is to improve the material's sensing performance. In this work, to study the sensing performance of the fractal sample, the homogenous slurry of the fractal material was coated uniformly over the glass substrate to form a thick film. Iso-propanol was used as a solvent for slurry preparation. Electrical contact pads were made on the glass substrate using highly conducting silver epoxy. The sensor was connected to the in-house developed gas sensing set-up. The sensor was exposed to ethanol vapors with 20 to 100 ppm concentration. The sensor was biased at 5V and all the testing was conducted at room temperature. Figure 3 shows the sensing response of the sensor for 20-60 ppm of ethanol concentration with (a) a change in resistance and (b) normalized percentage response values. The fast-sensing response is attributed to the unique

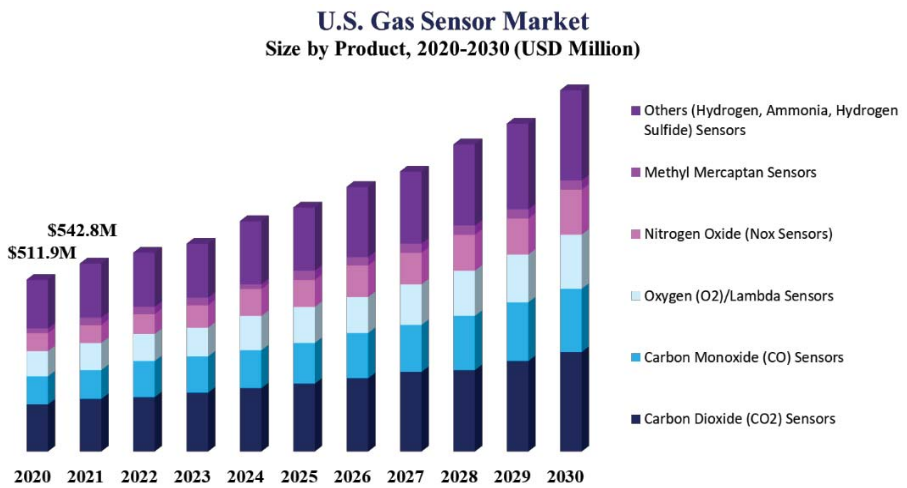

Figure 1: Recreated from 'Growth of US sensor market. Source: Grand view research, [1], available at https://www.grandviewresearch.com/industry-analysis/gas-sensors-market

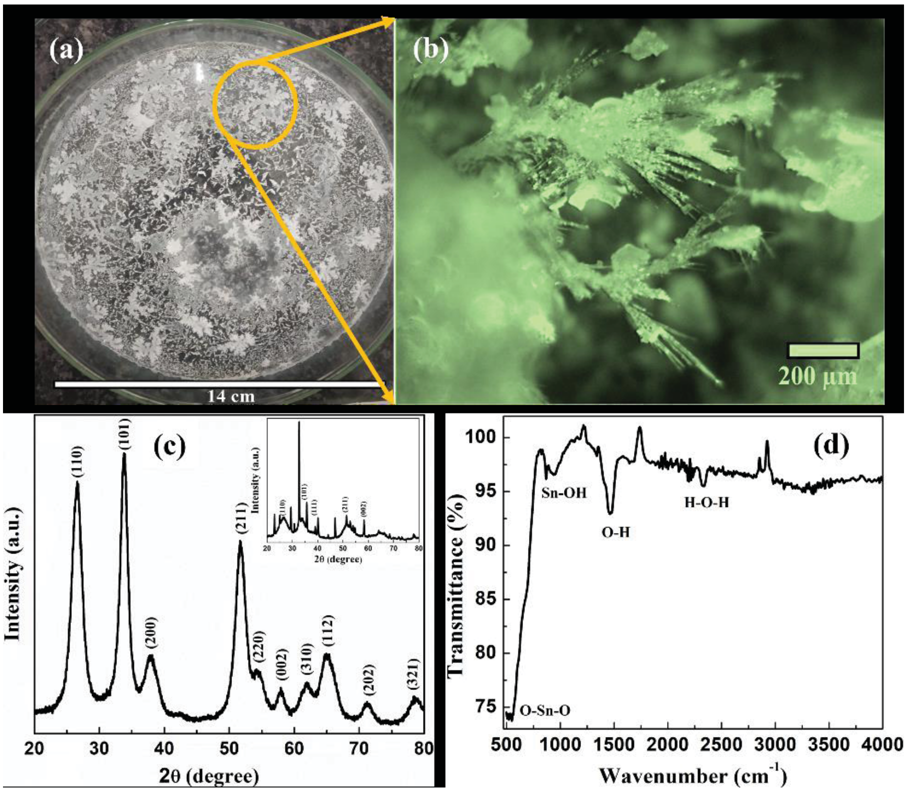

Figure 2: Tin oxide fractals grown on (a) large scale glass substrate, (b) digital optical image showing the dendritic growth, (c) x-ray diffractogram of annealed sample. Inset shows the x-ray diffractogram of as-synthesized fractal sample and (d) FTIR spectrum of tin oxide fractals.

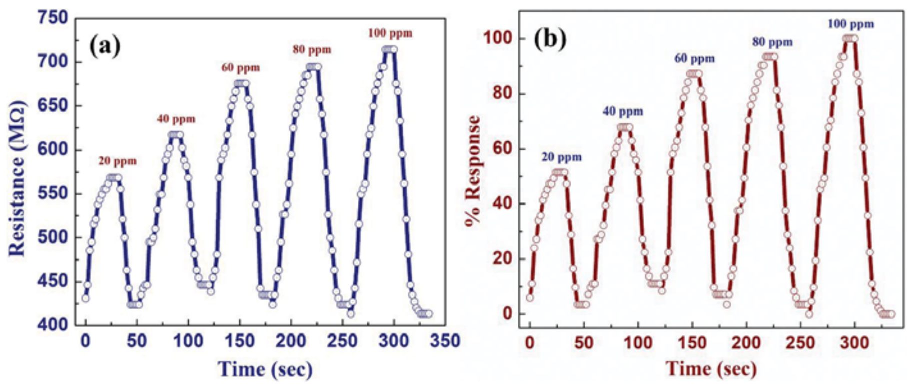

Figure 3: Sensing response of tin oxide sensor under ambient conditions (a) change in resistance of the sensor with exposed ethanol vapor concentration from 20-100 ppm (b) normalised percentage response for 20-100 ppm ethanol vapor concentration.

dendritic morphology of fractals which offer cross-connectivity between fractal fingers providing an electronically connected network of the sensing material, surface roughness, and abundant adsorption sites for interaction with target gas analytes [34,35]. The senor showed an average response time of ~18s ± 3s and an average recovery time of ~22s ± 5s at room temperature. In light of the foregoing, it is concluded that fractal morphology prepared using SnO_2 material at moderate conditions plays an important role in the sensing field because nano/micro scale fractal materials provide high porosity and surface area, high physical connectivity within patterned objects, and are an innovative way to improve sensing performance of known materials.

In summary, the sol-gel and microwave irradiation methods were used to obtain fractals with crystallite size of 45 ± 5 nm (as-synthesized) and 12 ± 2 nm (for annealed samples) as estimated from Scherrer's equation. The material successfully detected ethanol vapors in the range of 20-100 ppm concentration. The resulting material exhibited an average response time of ~18s ± 3 s and average recovery time of ~22s ± 5 s.

Conclusion

The gas sensing field is an active area of research. Whereas the sensor performance on substrates designed as fractals has been reported, reports on fractal material as sensing material are very few. This work demonstrates an innovative and facile synthesis methodology to mimic the nature and grow fractals of tin oxide. The material shows a great performance in sensing ethanol. This work highlights that apart from doping, band-structure engineering, nano-sizing, and raising the temperature, there is yet another unique way to enhance sensing performance by using fractals.

Acknowledgment

Author VK would like to acknowledge Symbiosis International (Deemed University) for a Senior Research Fellowship. The authors acknowledge the Symbiosis Centre for Research and Innovations (SCRI) for the Research Support Fund.

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How to cite this article: Nagar R, Kamathe V. Efficient Room Temperature Ethanol Vapor Sensing by Unique Fractal Features of Tin Oxide. IgMin Res. Feb 12, 2024; 2(2): 097-101. IgMin ID: igmin150; DOI: 10.61927/igmin150; Available at: www.igminresearch.com/articles/pdf/igmin150.pdf