

PAPER • OPEN ACCESS

Wavelength Dependent Ammonia Sensing Characteristics of SnO₂ based Fiber Optic Sensor

To cite this article: S Narasimman *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **360** 012055

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Wavelength Dependent Ammonia Sensing Characteristics of SnO₂ based Fiber Optic Sensor

S Narasimman¹, L Balakrishnan^{2*}, S R Meher³, R Sivacoumar⁴, Elizabeth Rufus⁴, and Z C Alex⁴

¹School of Electronics Engineering, VIT University, Vellore 632 014, India.

²Department of Physics, Government College of Technology, Coimbatore 641 013, India.

³Department of Physics, School of Advanced Sciences, VIT University, Vellore 632 014, India.

⁴Department of Sensor and Biomedical Technology, School of Electronics Engineering, VIT University, Vellore 632 014, India.

*Email: bslv85@gmail.com

Abstract. SnO₂ nanoparticles were synthesized by co-precipitation technique. The synthesized SnO₂ nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-visible diffused reflectance spectrometer (DRS). The XRD results addressed that the SnO₂ nanoparticles was crystallized in rutile tetragonal structure. The SEM analysis confirms that the prepared nanopowder is composed of nanoparticles. Analysis of the DRS UV-Vis spectrum showed that the band gap of the synthesized SnO₂ is to be ~3.4 eV. The small cladding portion of the optical fiber was replaced with the synthesized nanoparticles. The ammonia sensing characteristics of the prepared SnO₂ nanoparticles were analyzed for different wavelength ranges (red, yellow and blue) using polymethyl methacrylate fiber. It has been found that the synthesized SnO₂ nanoparticles shows high sensitivity (~23) in yellow wavelength range compared with red and blue wavelength ranges at room temperature.

Keywords: SnO₂, Nanopowder, Fiber optic sensor, Ammonia sensing, Wavelength dependent sensing.

1. Introduction

Ammonia (NH₃) has widespread use in chemical processes, living environment, medical treatments and industrial applications. Ammonia is an indispensable for many biological processes and serves as a precursor for amino acid and nucleotide synthesis. The amount of ammonia manufactured every year by human is almost equal to the amount produced by nature every year. Threshold limit of ammonia concentration in air is only 25 ppm for human beings. Generally, ammonia has been found in air, soil and water samples at hazardous wastes. About 80% of the manufactured ammonia is used as fertilizer in agriculture and also used to manufacture synthetic fibers, plastics and explosives. Still, ammonia is a toxic gas and severe irritant to the respiratory system. Generally, the minimum explosive limit for ammonia is 15% [1]. Depending on those conditions and sensibilities, the critical requirement of flexible and effective ammonia monitoring everywhere is hurried. Metal oxides based ammonia gas sensors are being developed extensively as they are highly sensitive to NH₃ and also easy to



materialize [2]. These sensors are traditionally of the electrical resistive whose resistance varies when they are exposed to the detecting gas. However, these sensors exhibit enhanced gas sensitivity only at high operating temperatures (above 200 °C) and also respond to many gases (CO, NH₃ and methanol) [3,4]. In the recent decades, fiber optic gas sensors based on metal oxides as the sensing medium have been reported for improving gas sensitivity and selectivity for room temperature operation. These sensors are immune to electromagnetic interference, low cost and could be used in the hostile environments [5,6]. The gas sensing technique is based on cladding transition technology, in which a centre portion of clad in the optical fiber is denuded and coated with the gas sensing material. The intensity of the light passing through the fiber is very sensitive to the change in the refractive index of the sensing medium which gets changed due to gas species interaction [7].

In this article, the fiber-optic sensing surface is prepared by modifying the original cladding material with a chemical sensitive material, SnO₂ on a certain portion of optical fiber. We have studied the wavelength dependent ammonia sensing characteristics of SnO₂ nanoparticles at different gas concentrations.

2. Experimental Details

SnO₂ nanopowders were synthesized by co-precipitation technique. Tin (II) chloride (SnCl₂) was used as a precursor, tri-ethanolamine (C₆H₁₅NO₃) act as a solvent and ammonia is used as precipitating agent respectively. For the synthesis of SnO₂ nanopowders, 25 ml of 0.2 M tin (II) chloride and 25 ml of 0.5 M tri-ethanolamine solutions were prepared. Initially, tin (II) chloride and tri-ethanolamine were mixed and stirred continuously for 5 hr. Then, the aqueous ammonia solution was added to the mixed solution drop wise for 1 hr. After adding a particular amount of ammonia, the precipitation starts and the concentrations of precipitates increases as the addition was increased. Till the p^H of the solution reaches 8.0, ammonia was added. Further, the solution was stirred for another 30 min and then the particles were washed with double distilled water to remove the residual ions then filtered with filter paper. Finally, the powder was calcined at 600 °C for 4 hr.

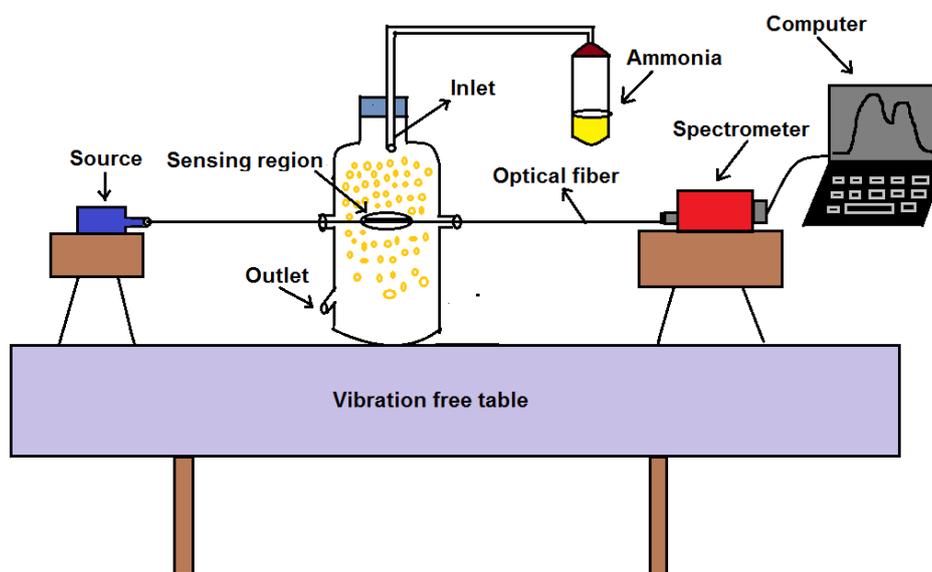


Figure 1. Fiber optic gas sensing setup.

Figure 1 shows the scheme of fiber optic gas sensing setup used for the present study. The sensor consists of multimode step index plastic fiber having a length of 42 cm, diameter of 750 μm and numerical aperture of 0.51. The refractive index of the core and cladding are 1.492 and 1.402, respectively [8,9]. The fiber is made up of polymethyl methacrylate and is cleaved at both ends, and coupled with light source and spectrometer. The sensor setup contains a broadband light source

(Halogen light source-SLS201/M) with the wavelength range from 300 to 2600 nm and fiber optic spectrometer (CCS200/M) having a spectral response of 200 to 1000 nm. In a middle portion of an optical fiber, the sensing region was formed by abolishing mechanically the original cladding of the fiber up to the core for a length of 3 cm. Initially, the buffer was cleaved. Then the original cladding surface was etched away using acetone solution. The etched surface was cleaned and coated with sensing material to serve as a new cladding. The SnO₂ nanopowder was mixed with double distilled water to form a paste and coated in the clad removed region by dip coating method as new cladding [10]. At different wavelength ranges for different concentrations of ammonia the intensity variations were recorded using spectrometer interfaced with computer. The sensor studies were carried out under normal atmosphere pressure and room temperature.

3. Results and Discussion

The X-ray diffraction pattern of SnO₂ nanopowders are shown in the Figure 2. The XRD pattern of the synthesized SnO₂ nanopowders could be addressed to rutile tetragonal structure (PCPDF card no-88-0287). The sharp and narrow diffraction peaks corresponds to (110), (101), (111) and (211) different planes confirms the formation of rutile structured nanopowder [11]. There is no impurity phases was detected within the XRD detection limits.

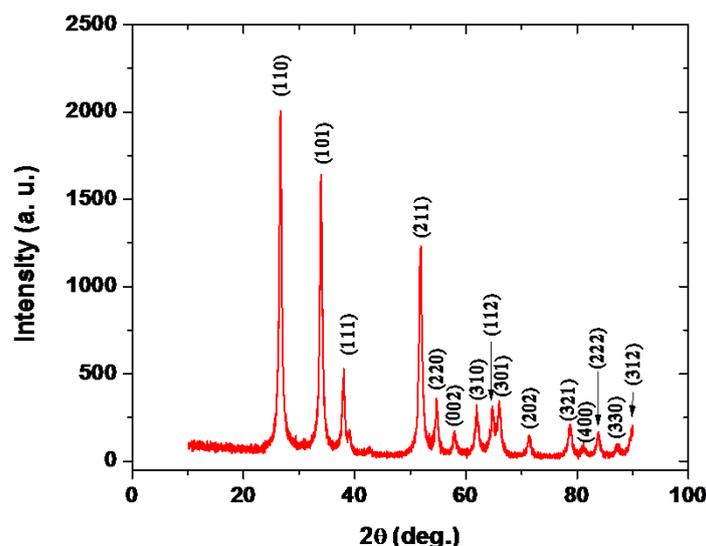


Figure 2. XRD pattern of synthesized SnO₂ nanopowders.

The average crystallite size of the nanopowders are estimated as ~29 nm from Williamson and Hall (W-H) equation for Cauchy-Lorentzian is given by [12],

$$\beta \cos \theta = \frac{C \lambda}{D} + 4 \varepsilon \sin \theta \quad (1)$$

where, D is the crystallite size, C is the shape factor usually taken to be 0.89, β is full width at half maximum (FWHM), θ is Bragg diffraction angle and λ is the wavelength of radiation ($\lambda=1.54 \text{ \AA}$). Figure 3a and 3b shows the surface morphology of the SnO₂ nanopowders at different magnification. It exhibits the formation of spherical shaped nanoparticles having an average size of 275 nm which are uniformly distributed.

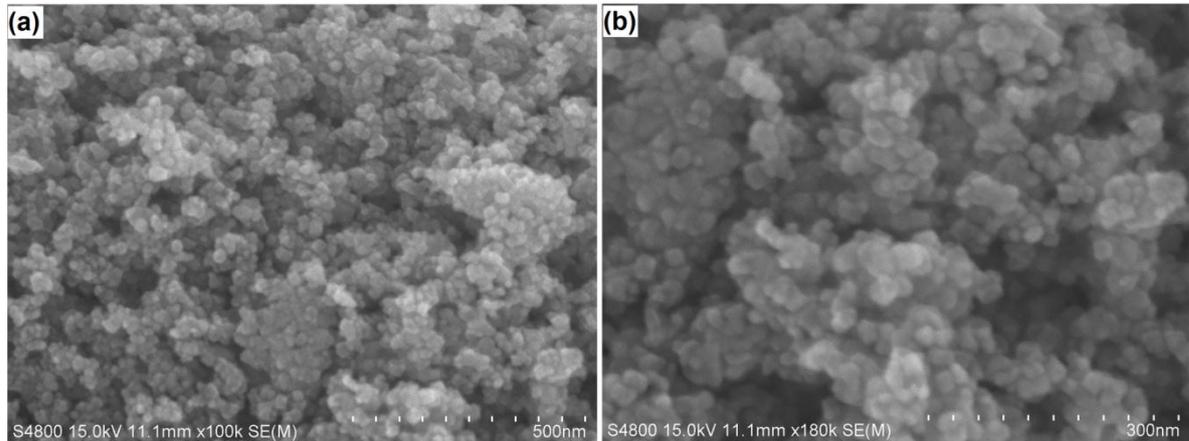


Figure 3. SEM micrographs of SnO₂ nanopowders at two different magnification (a) 500 nm and (b) 300 nm.

The optical absorption of the synthesized SnO₂ nanopowders is given in Figure 4a. It shows strong absorption in the visible region (285 nm). The energy band gap of the sample was examined by Tauc's relation. According to this relation, the absorption co-efficient is given by,

$$\alpha(h\nu) = C(h\nu - E_g)^m \quad (2)$$

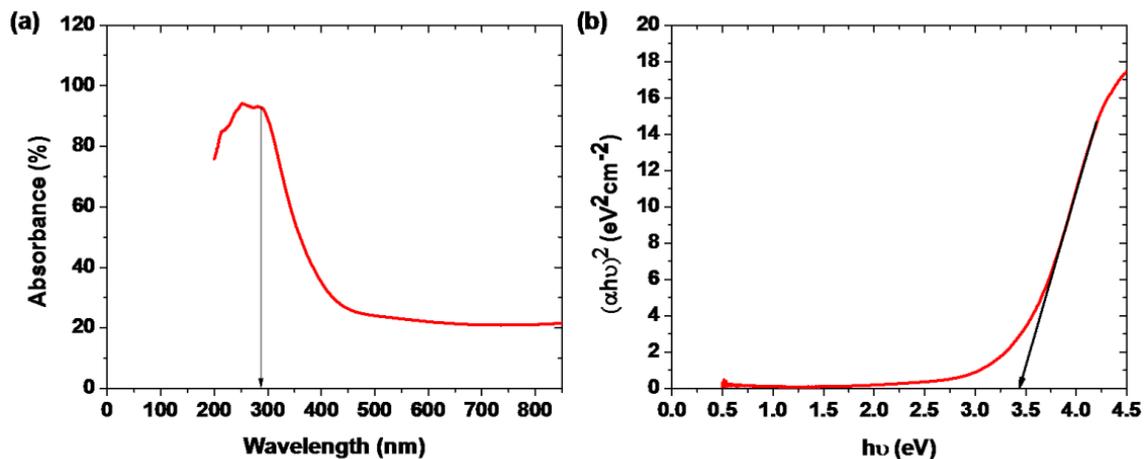


Figure 4. (a) Absorption spectra of SnO₂ nanopowders and (b) Tauc's plot.

where, C is a constant, E_g is the energy gap, $h\nu$ is the photon energy and m is an exponent which assumes the value depends on the electronic transition. In order to determine the optical energy gap of the SnO₂ sample, the graph of $h\nu$ versus $(\alpha h\nu)^2$ has been plotted by replacing $n=1/m$ where m takes the value of 2 for allowed direct transition [13]. From Figure 4b, the value of band gap for the prepared SnO₂ nanopowder was found as ~ 3.4 eV.

The optical fiber works on the principle of total internal reflection between core and cladding. Generally, the light intensity is not fully reflected but a small amount of light intensity pierces into the cladding region and its intensity decays exponentially away from the interface (it is called evanescent field) [14]. The cladding region which is having refraction index of 1.492 was replaced with the

sensing material having refractive index of 2.0. In such condition the fiber will operate in leaky mode. The change in output characteristics may be attributed to the change in refractive index of new cladding region which may increase or decrease from 2.0.

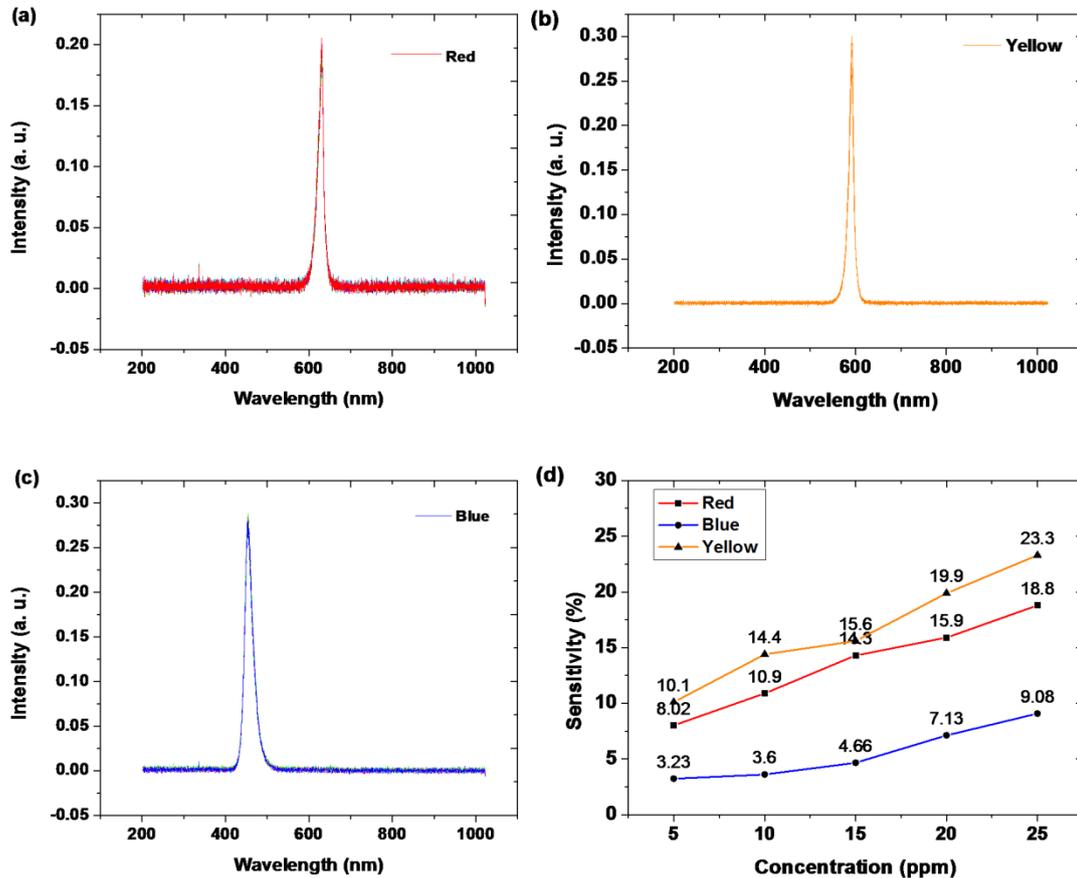


Figure 5. Spectral response and sensitivity of SnO₂ nanopowders for various concentration of ammonia at different wavelength ranges (a) Red (b) Yellow and (c) Blue. (d) Variation of sensitivity at different concentration of ammonia and at different wavelengths.

Figure 5a, 5b and 5c shows the output spectral characteristics of SnO₂ nanopowders upon exposure to different concentration (0 to 250 ppm) of ammonia at room temperature. The spectra exhibits sharp peak for different LEDs of red, yellow and blue around 620 nm, 588 nm and 450 nm, respectively. This peak intensity expresses large variation with the concentration of the gas.

The sensitivity was calculated using the given formula [15],

$$S(\%) = \frac{|R_{\text{gas}} - R_{\text{air}}|}{R_{\text{air}}} \quad (3)$$

where, R_{air} is the intensity in air ambience and R_{gas} is the intensity in presence of gas. The ammonia sensing properties of the clad modified fiber was studied at different wavelength of 620 nm, 580 nm and 450 nm for red, yellow and blue LEDs, respectively. From the Fig. 5d, it is seen that for all the

gases sensitivity increases with the increase in concentration and shows highest sensitivity (~23) in yellow wavelength range compared with red and blue wavelength ranges at room temperature.

4. Conclusion

The rutile structured SnO₂ nanopowders were synthesized by co-precipitation method. The SEM image showed the formation of spherical shaped nanoparticles with the average size of 275 nm. The spectral characteristics of fiber optic sensor for the detection of ammonia in different wavelength ranges (red, yellow and blue) were studied at room temperature. It shows linear increase in sensitivity for all the wavelengths with increase in ammonia concentration. It has been found that the synthesized SnO₂ nanoparticles shows highest sensitivity (~23) in yellow wavelength range compared with red and blue wavelength ranges. This study clearly demonstrates that the fiber optic sensor works successfully for the detection of ammonia using SnO₂ as the modified cladding material in yellow wavelength region.

References

- [1] Agency for Toxic substances and Disease Registry (ATSDR) 2004 Toxicological profile for ammonia. Atlanta GA:U.S. Department of Health and Human Services Public Health Service
- [2] Pourfayaz F, Khodadadi A, Mortazavi Y, and Mohajezadez S S 2005 *Sens. Actuators, B* **108** 172
- [3] Zhang M, Yuan Z, Song J, and Zheng C 2010 *Sens. Actuators, B* **148** 87
- [4] Ahmed F, Arshi N, Anwar M S, Danish R, and Koo B H 2013 *Curr. Appl. Phys.* **13** 64
- [5] Fernandez Vallejo M, and Lopez Amo M 2012 *Sensors* **12** 3929
- [6] Cao W and Duan Y 2005 *Sens. Actuators, B* **110** 252
- [7] Xu J, Han J, Zhang Y, Sun Y A, and Xie B 2008 *Sens. Actuators, B* **132** 334
- [8] Huang J, and Wan Q 2009 *Sensors* **9** 9903
- [9] Yuan J, and El-Sherif M A 2003 *IEEE Sens. J.* **3** 05
- [10] Vijayan A, Fuke M, Hawaldar R, Kulkarni M, Amalnerkar D, and Aiyer R C 2008 *Sens. Actuators, B* **129** 106
- [11] Tian Z M, Yuan S L, He J H, Li P, Zhang S Q, Wang C H, Wang Y Q, Yin S Y, and Liu L 2008 *J. Alloys Compd.* **466** 26
- [12] Zak K, Abd. Majid W H, Abrishami M E, and Yosefi R 2011 *Solid State Sci.* **13** 251
- [13] Yang J, Wang Y, Kong J, Yu M, and Jin H 2016 *J. Alloys Compd.* **657** 261
- [14] Morisawa M, Amemiya Y, Kohzu H, Liang C X, and Muto S 2001 *Meas. Sci. Technol.* **12** 877
- [15] Liu X, Chen N, Han B, Xiao X, Chen G, Djerdz I, and Wang Y 2015 *Nanoscale* **7** 14872

Acknowledgments

The authors express their sincere thanks to Department of Science and Technology (DST), New Delhi, India for providing the financial support through FIST (Fund for Improvement of S&T Infrastructure in Higher Education Institution) project [SR/FST/ETI-015/2011].