



Annealing-induced enhancement of TiO₂-ZnO nanocomposites for high-performance room-temperature air pollutant detection in fiber optic sensors

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ARTICLE INFO

Keywords:

Fiber optic sensor
TiO₂ doped ZnO
Room environment sensor
Cladding modification
Gas selectivity
Inorganic and VOC gases

ABSTRACT

Fiber optic sensors, promising for their compactness and remote sensing abilities, are explored in this study as a platform for detecting volatile organic compounds (VOCs) using nanocrystalline metal oxide composites like TiO₂-doped ZnO. Hydrothermally synthesized (S1 sample) and annealed composites (500 °C (S2 sample) and 1200 °C (S3 sample) annealing) were investigated for their gas-sensing properties towards inorganic gas like ammonia and VOCs like acetone, and isopropyl alcohol. Remarkably, annealing at 1200 °C yielded S3 sample with higher response (7.5 %) towards ammonia at room temperature for 500 ppm concentration. This superior performance is attributed to increased surface area, narrowed bandgap, and faster response/recovery times (18/15 s) compared to other samples. The proposed sensing mechanism involves the adsorption and desorption of oxygen molecules on the sensor surface, altering refractive index and light scattering, ultimately modulating the transmitted light intensity. X-ray diffraction, SEM imaging, and UV-Vis absorption techniques confirmed the structure and morphology of the nanocomposites.

1. Introduction

To meet the requirements of an expanding population and overall economic growth in industries, there has been a need for tremendous growth in fiber optic communication and optoelectronic industries which led to the development of fiber optic-based sensors [1–3]. These fiber optic sensors operate by measuring variations in guiding light properties such as amplitude, time, frequency, and polarization [4]. Optical fiber sensors provide intrinsic benefits over conventional sensing technologies, including improved sensitivity, compact mass and weight, and resistance to electromagnetic interferences [5]. As a result, the scientific community devotes all of its resources and expertise to the development of a superior gas monitoring material that can operate at standard atmospheric temperature and pressure [6]. Traditionally,

Metal oxide and doped semiconductors (MOS) are said to have a potential function in gas sensing due to their superior electrical properties [7,8]. Research fraternity has explored that noble metals modified MOS could exhibit enhanced gas-sensing performance. Noble metals, on the other hand, are prohibitively expensive and scarce, making their widespread use difficult [9]. In recent times, many researchers have reported on mixed and doped metal oxide nanocomposites, as the chemical interaction between two metal oxides can result in the formation of new active sites and enhanced surface area which encourages improved catalytic, gas sensing mechanisms [5,10–13].

Because of their physical and chemical stability, straightforward synthesis process, low cost, and abundant existence in nature, metal oxide semiconductors have always sparked scientists' interest [7,14–16]. ZnO, an n-type semiconductor, is one such versatile material,

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<https://doi.org/10.1016/j.microc.2024.110329>

Received 9 November 2023; Received in revised form 13 February 2024; Accepted 13 March 2024

Available online 14 March 2024

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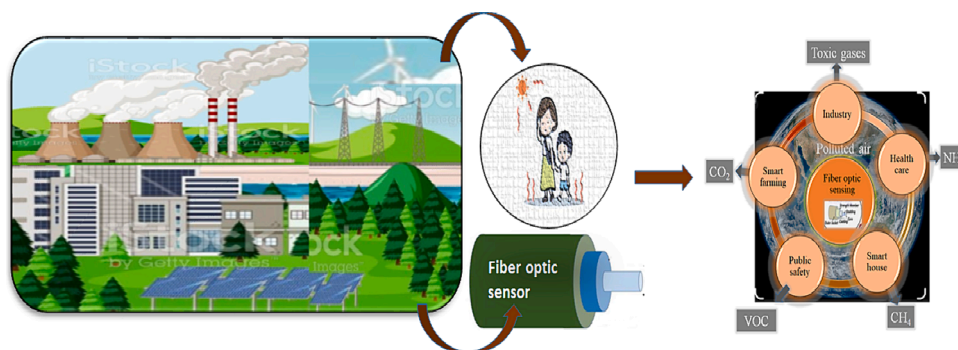


Fig. 1. Visual representation of Fiber optic gas sensors for VOC detection in various applications.

Table 1

Details of sample code.

S.No	Sample	Code
1.	As prepared TiO ₂ -ZnO	S1
2.	TiO ₂ -ZnO annealed at 500 °C	S2
3.	TiO ₂ -ZnO annealed at 1200 °C	S3

utilized in gas sensing applications, owing to its excellent thermal stability, resistance to extreme environmental conditions, and catalytic properties. However, when dealing with pollutants, the biggest drawback of ZnO is its huge band gap and constrained light absorption range [17]. To enhance the ZnO host's gas sensing capabilities, many modifications have been made to enhance the functional property of the ZnO structure, either by the addition of any dopants or using hybrid semiconductors such as SnO₂, TiO₂, etc to form nano-composites. In addition, it is believed that the coupling of semiconductor oxides provides a circumstance that permits advantageous redox reactions with the absorbed surface species, thus supporting the sensing property. Given

that ZnO and TiO₂ have almost similar conduction bands and valence bands, their formation is made simple by the ease of electron-hole transfer [18].

In this study, solid-state TiO₂ doped ZnO nano-composites synthesized via hydrothermal route were employed as clad modified fiber optic sensing materials for VOC gas detection, including ammonia, acetone, and *iso*-propyl alcohol (IPA). Further, our group have previously studied on ammonia sensing properties on ZnO [19,20] and TiO₂ [15] metal oxide separately using clad modified fiber optic sensors, however no much reports are available upon sol-gel synthesized TiO₂ doped ZnO wherein, the gas sensing potential is analysed upon the as-prepared composite and the annealed samples at various temperatures (500 °C & 1200 °C) to study the effect of annealing on fiber optic gas sensors at ambient temperature (Fig. 1).

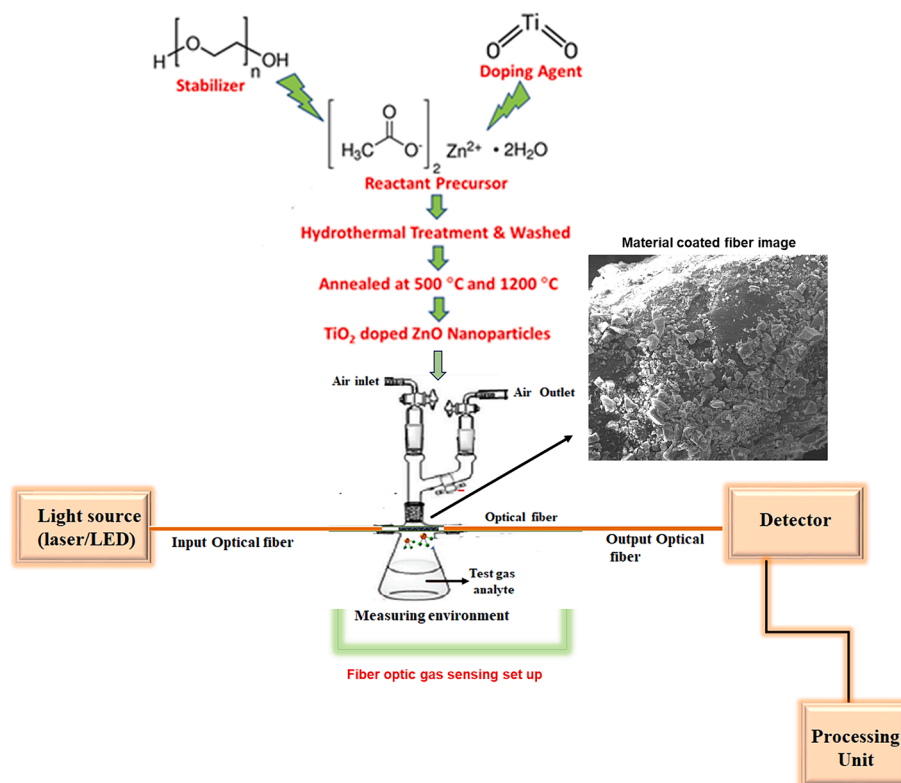


Fig. 2. Schematic representation of Sample coated fiber optic gas sensor.

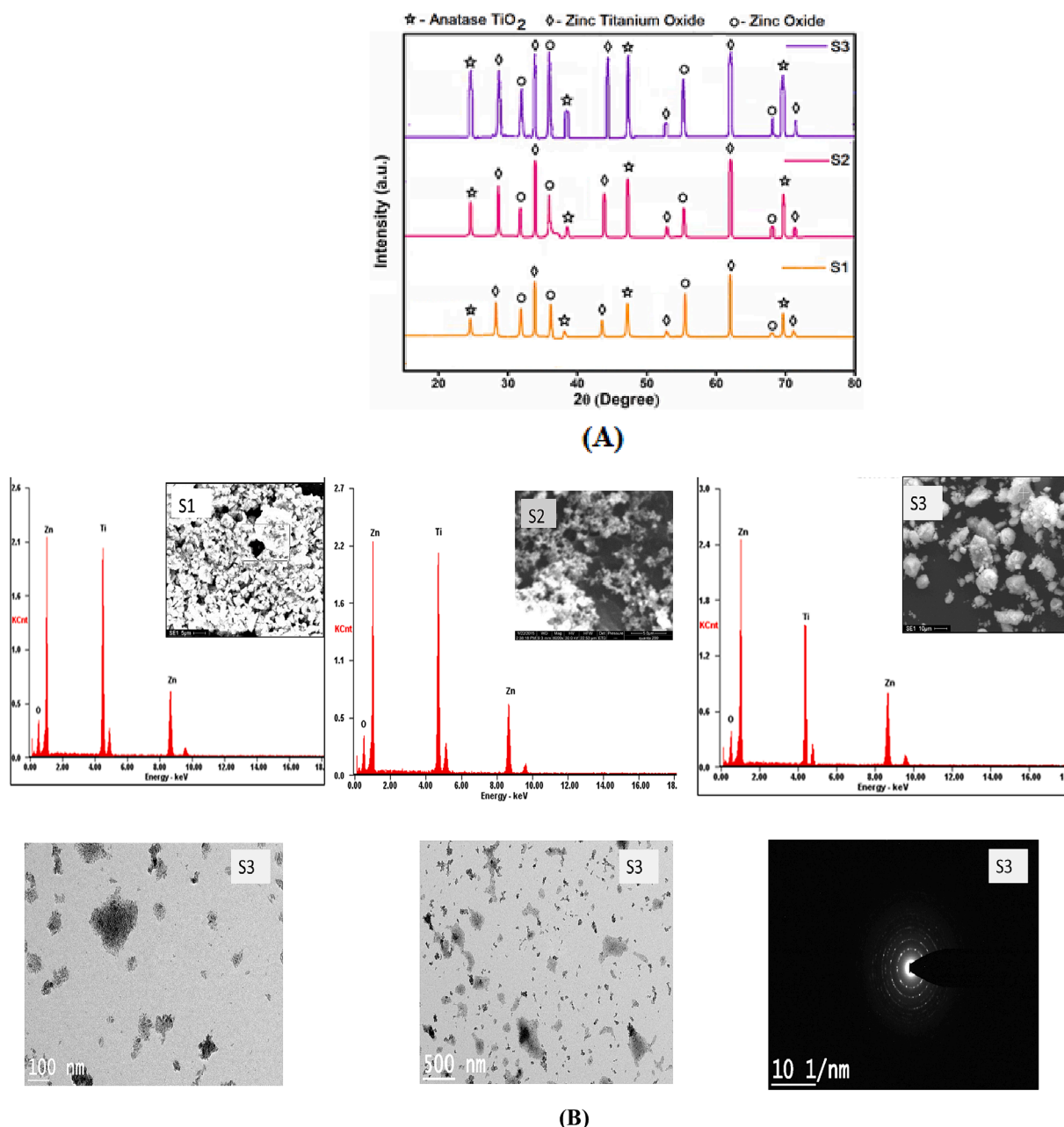


Fig. 3. (A) Structural analysis of samples using XRD. (B) EDS analysis of samples with SEM images in the inset and HRTEM analysis of S3 samples with its respective SAED pattern.

2. Experimental setup

2.1. Material synthesis and characterization study

For the synthesis of $\text{TiO}_2\text{-ZnO}$ nano-composites, the necessary precursors that were purchased from Alfa Aesar were Zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], Titanium tetra isopropoxide (TTIP), polyethylene glycol (PEG), ethanol, double distilled water. Zinc acetate and TTIP were used as sources, while polyethylene glycol (PEG) and double distilled water were used as solvents respectively. The desired amount of zinc acetate was mixed into PEG under strong stirring to obtain solution A. Similarly desired quantity of TTIP was mixed in double distilled water and was left for continuous stirring to obtain as solution B. Solution B was mixed into solution A very carefully in the ratio of 1:1 under vigorous stirring for nearly two hours to obtain a pale yellow solution. After mixing, the solution was transferred to a hydrothermal synthesis

system for 2 h at 120 °C. After cooling, the mixture was washed five times with ethanol and was dried at 100 °C for 4 h. The as-synthesized $\text{TiO}_2\text{-ZnO}$ nano-composites were further annealed at 500 °C and 1200 °C in a muffle furnace at a ramp rate of 5 °C/min. The synthesized samples were subsequently examined for their morphology, elemental characteristics, and structural analyses using a scanning electron microscope (SEM) (Zeiss EVO 18, Germany), High Resolution Transmission Electron Microscope (HR-TEM) (Jeol/ JEM 2100) at a working voltage of 200 kV, and XRD (Model: D8 Advance, BRUKER, Germany) respectively. The samples synthesized are named henceforth as [Table 1](#).

2.2. Gas sensing set up using PMMA optical fiber

The gas sensing setup used a 30 cm long PMMA multimode optical fiber that was very carefully etched at the center for about 3 cm of the cladding region such that the core region was left unharmed. To measure

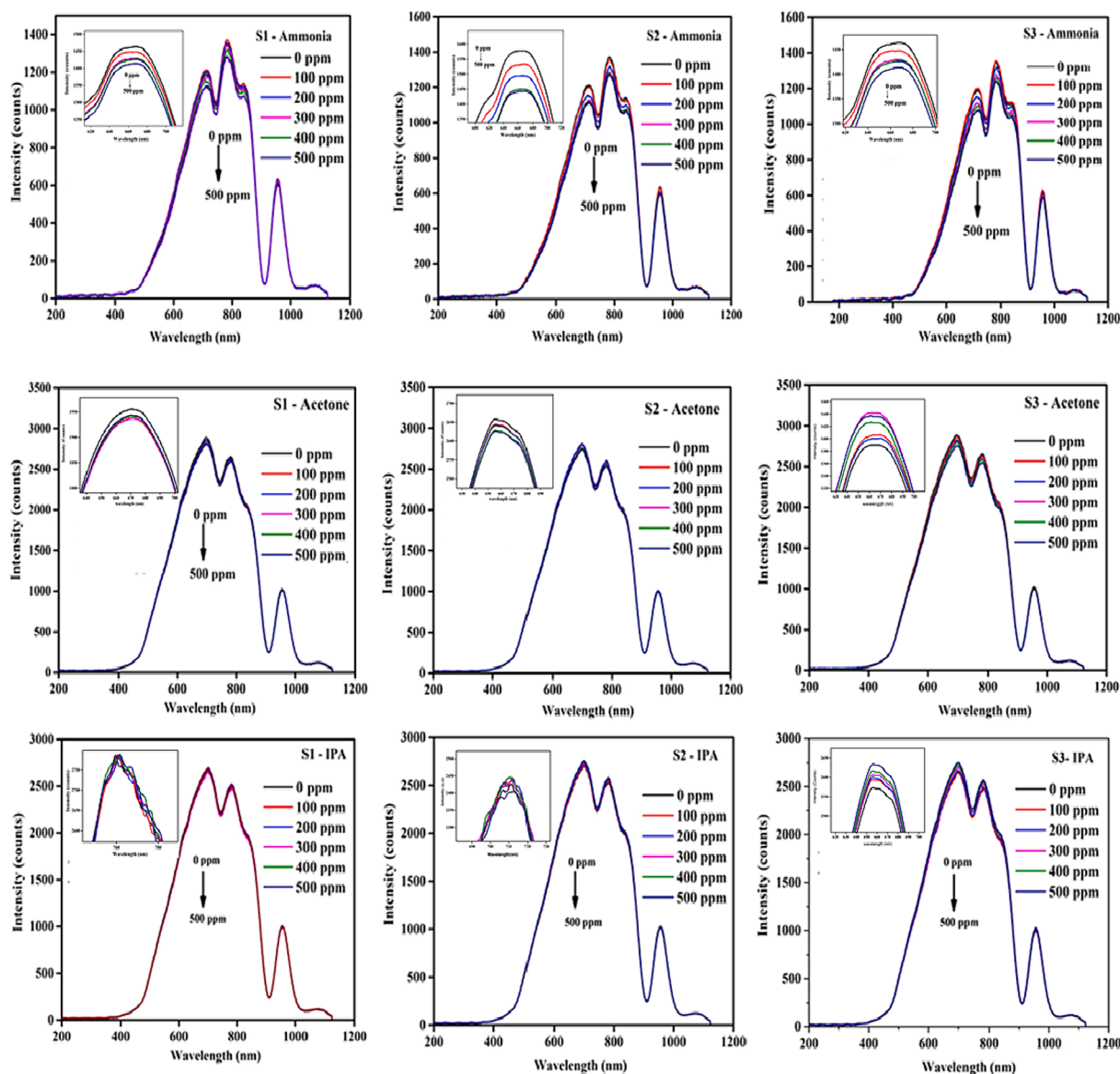


Fig. 4. Spectral response of samples S1, S2 and S3 exposed to test gases at room temperature.

the intensity of different test gases that were permitted to enter the sensor, the setup makes use of a light source and a detecting spectrometer interfaced to a laptop intended to record the spectral intensity [21]. The synthesized $\text{TiO}_2\text{-ZnO}$ nano-composites and the annealed nano-composites were made into a slurry paste and were coated upon the clad cleaved region using a dip coating route thus acting as the clad modified sensing head. The thickness of the clad engraved region was determined using an HMV-2 make Micro hardness tester and was found to be $\sim 75\ \mu\text{m}$ before coating and $\sim 110\ \mu\text{m}$ after coating. The thickness of the coating for all three samples was maintained uniformly throughout the experiment. Meantime, the test gas solutions of ammonia, acetone, and IPA solutions were prepared from 100 to 500 ppm with a step increment of 100 ppm using the serial dilution factor method. The prepared gas solution was then taken in a glass beaker in such a manner that the gas vapor from each test gas solution was allowed to interact with the $\text{TiO}_2\text{-ZnO}$ clad modified region of the PMMA optical fiber at room temperature. The vapors were entrained in an air stream with a flow rate of 1 L/min and pressure of 101.383 kPa and directed into the gas chamber. To stabilize the gas inside the chamber, the output spectral response of the sensor was recorded for each concentration at intervals of ten minutes. The entire experiment

was carried out for all three samples S1, S2, and S3 in a dark room at a room temperature of about $30\ ^\circ\text{C}$ and constant relative humidity of about 50 %. From the output spectral response that was recorded, a graph was plotted for each concentration of test gas solution, to determine the gas sensitivity. Further, the control of sensitivity to varied humidity was also analyzed by varying the humidity (15 % – 50 %) of the laboratory using an impeller humidifier within the environmental chamber specifically designed for humidity control, for S3 at a concentration of 500 ppm. The gas chamber operates as an internal circulation system, ensuring isolation from the laboratory's ambient humidity fluctuations. This ensures that the target gas concentration of 500 ppm remains stable and unaffected by external factors. The time response analysis was also performed for the sample with the highest sensitivity. The schematic representation of the fiber optic setup is displayed in Fig. 2.

3. Results and discussion

3.1. Material characterization (XRD, SEM, and TEM analysis)

Powder X-ray diffraction experiments were carried out upon the TiO_2

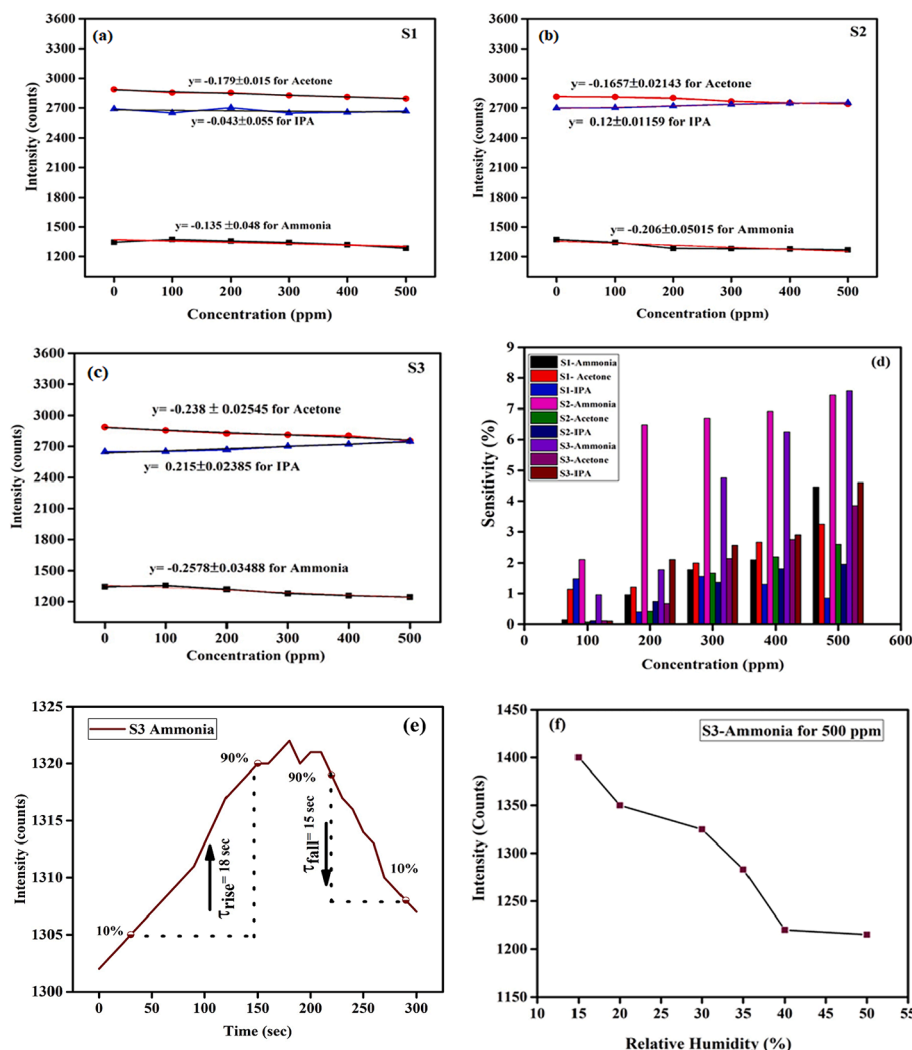


Fig. 5. (a-c) Gas sensitivity measurement for the samples in the presence of test gas solutions, (d) Sensitivity percentage measurement to determine its selectivity, (e) Time response analysis of S3 towards ammonia at 500 ppm, (f) Response analysis of S3 based ammonia sensor under different Relative humidity.

Table 2

A comparative analysis of various doped ZnO with target ammonia gas.

Gas sensing material	Synthesis	Concentration	Sensitivity (%)	Gas response and operating temperature	Reference
Al (3 %) doped ZnO	Spray Pyrolysis	25 ppm	–	26 sec at 100 °C	[24]
Zr (3 %) doped ZnO	Successive ionic layer adsorption and reaction (SILAR)	25 ppm	7130	48 sec at Room temperature	[25]
Cu functionalized ZnO	Wet chemical synthesis	100 ppm	14.52	15 sec at Room temperature	[26]
Cr (2 %) doped ZnO	Nebulizer spray pyrolysis	200 ppm	–	67 sec at Room temperature	[27]
rGO/ZnO	Spray Pyrolysis	50 ppm	3.05	84 sec at Room temperature	[28]
TiO ₂ Doped ZnO Annealed at 1200 °C	Wet Chemical synthesis	500 ppm	7.5	18 sec at Room temperature	Present Work

doped ZnO nano-composites using a Rigaku diffractometer (Model: Ultima III, Japan) and CuK α (1.54 Å) radiation, to assess crystallite size, determine the sample's phase, and see if the annealing temperature had any effect on the size of the particles. Fig. 3(A) displays the XRD pattern of samples both before and after heat treatment. XRD revealed that upon annealing the samples, the peak intensity began to increase up to 1200 °C, which in turn increases their crystallinity. Further, the peaks revealed phases of TiO₂, Zinc titanium oxide, and zinc oxide present in the samples, with a very minor shift in the peak intensity towards greater angles. The grain size of the samples was estimated with Scherrer's formula and was found to be 13, 23, and 31 nm for the S1, S2,

and S3 samples respectively.

Fig. 3(B) displays the morphological analysis via Scanning electron microscope of the samples S1, S2, and S3, which revealed that there was an agglomeration of the nanoparticles upon heat treatment for S2 and S3. The cause might be the coalescence of small grains brought on by the increased kinetic energy at high temperatures, which brings about more oxygen vacancies needed for improved gas sensing [22]. Further EDS analysis of the samples displayed the presence of Zn, Ti and O in the samples. The EDS spectra of S3 showed a decrease in Ti and O peaks compared to other two samples, which could be due to the effect of thermal treatment which reduces the anatase content in TiO₂ and

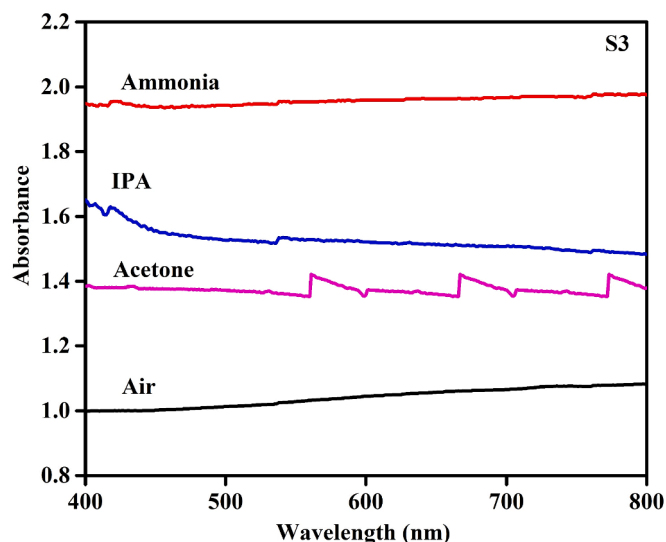


Fig. 6. The Absorbance spectra of S3 sample in air, ammonia, acetone and IPA test gas environment at room temperature.

increases the oxygen vacancy concentration as the calcination temperature is raised [23]. The TEM analysis was performed for sample S3 as it exhibited higher crystallinity as shown in Fig. 3(B). The TEM revealed that the nanoparticles have a crystalline size of 20–30 nm, which is consistent with the XRD observations. The SAED pattern reveals the crystalline nature of nanoparticles by a large number of brilliant spots.

3.2. Fiber optic gas sensing analysis

3.2.1. Spectral response analysis

All of the samples are subjected to vapors of solutions ranging from 0 to 500 ppm of test gases ammonia, acetone and iso propyl alcohol (IPA). The needed concentrations of ammonia, acetone and iso propyl alcohol are prepared via serial dilution method, and vapors are circulated throughout the chamber at room temperature. Fig. 4 exhibits the output response and spectral properties of a sensor for test gas solutions fitted with TiO_2 doped ZnO clad modified optical fiber. It was observed that wavelength of all the peaks were characteristic to PMMA optical fiber, however the intensity of light varied for all the samples based on their concentration of test gas solutions.

At ambient temperature, the spectral responses of nanocrystalline materials exposed to these test gas solutions at concentrations ranging from 0 to 500 ppm were measured. From Fig. 4, it is clearly depicted that the output spectral characteristics of TiO_2 doped ZnO annealed at 1200°C (S3) sample revealed enhanced sensing response compared to S1 and S2 samples, when exposed to varied concentrations of ammonia, acetone and IPA test gas solutions. Furthermore, S3 exhibited better response towards ammonia gas solution compared to other test gas solutions at room temperature and constant relative humidity. The spectrum exhibited peaks at 690 nm, 767 nm and 957 nm characteristic to PMMA optical fiber. The intensity of the peaks clearly confirmed that sensing property has an impact upon annealing the samples to higher temperature.

3.2.2. The Sensitivity, selectivity and time response analysis

One critical parameter that determines the gas sensing response is the gas sensitivity, which is determined by the variation in the intensity of light as a function of the gas concentration which is measured in terms of ppm. Fig. 5(a-c) depicts the normalized gas sensitivity for S1, S2, and S3 samples towards acetone, ammonia, and IPA solution, which is typically the slope of the linear plots. The gas sensitivity slopes were calculated for spectral peak intensities at 690 nm along the y-axis and

concentration of test gas solution along the x-axis for all the samples and was found that for S1 samples the slopes obtained were found to be -0.179 ± 0.015 for acetone, -0.043 ± 0.055 for IPA and -0.135 ± 0.048 for ammonia. Likewise, the gas sensitivity slopes for S2 were found to be -0.1657 ± 0.02143 for acetone, 0.12 ± 0.01159 for IPA, -0.206 ± 0.05015 for ammonia, and for the S3 sample, the slopes were measured to be -0.238 ± 0.025 for acetone, -0.215 ± 0.023 for IPA and -0.257 ± 0.034 for ammonia respectively. From the slopes, it was observed that the TiO_2 -ZnO nano-composites upon annealing to higher temperature exhibited better sensitivity at room temperature compared to as prepared sample. Further, the selectivity measurement was performed by calculating the sensitivity percentage of the samples as shown in Fig. 5(d) using the formula $\text{Sensitivity (\%)} = (I_0 - I_g / I_0) * 100$, where the intensity of light at 0 ppm is referred as I_0 , and intensity of light from 100–500 ppm is I_g . The results demonstrated that the maximum sensitivity percentage of about 7.5 % appeared for S3 samples towards ammonia for 500 ppm at room temperature.

Further temporal response and recovery tests were carried out on the annealed S3 sample since an ideal gas sensor should have improved sensitivity, great linearity, and a quick response time. Fig. 5(e) shows the temporal response characteristics of the sensor for S3 in ammonia. It is reversible to a large extent. The time it took for the sensor signal (at 690 nm) to rise from 10 % to 90 % of maximum intensity and then fall from 90 % to 10 % of maximum intensity was used to calculate the response time. The response and recovery times were found to be approximately 18 and 15 s, respectively.

The gas sensing capabilities of gas sensors in real-world applications are typically severely impacted by relative humidity (RH). Therefore, research on how environmental RH affects the gas sensor is required. In this regard, the effect of Relative humidity ranging from 15 % to 50 % on the gas sensing performance of the S3 sample to detect ammonia was studied as shown in Fig. 5(f). It is clearly observed that the spectral response of the S3-clad modified fiber optic sensor to 500 ppm of ammonia gradually reduced as the humidity increased. The lower chemical adsorption of oxygen species on the surface of the sensing material caused by the adsorption of water molecules at high RH may be responsible for the decrease in spectral response under high relative humidity. Table 2 compares the sensing capabilities of the present material with various doped ZnO for ammonia sensors reported in the literature.

3.3. UV absorption spectra

Utilizing a UV spectrophotometer, the absorption spectra of the S3 samples were examined to evaluate the experimental settings in air, IPA, acetone and ammonia at room temperature (RT). UV-Vis absorption study was performed by coating the sample on one of the inner walls of the cuvette and pouring almost 1 ml of the solution (IPA, acetone and ammonia) in its bottom at a time for the vapour to evaporate. Neither the solution nor the coating came into contact. For comparison, a similar cuvette with sample coating was taken as reference without any solution poured in it as air medium and the spectra were recorded. The solutions were allowed to vaporize for 10 min after the cuvettes' open ends were closed with Teflon closures. The absorption spectra of S3 sample (annealed at 1200°C) in ammonia, IPA, acetone and the air test environment are shown in Fig. 6. The result depicts a clear increase in the absorbance for ammonia (~1.9), compared to IPA (~1.6), acetone (~1.4), and air environment (~1.0), with roughly the same light absorption in the 400–800 nm spectral range where the sensor response is detected. Ammonia exhibited highest absorbance compared to other test gases, which could be due to the enhanced interaction with the sensing material [29].

3.4. The proposed sensor's gas sensing mechanism

The proposed gas sensor basically works on the principle of

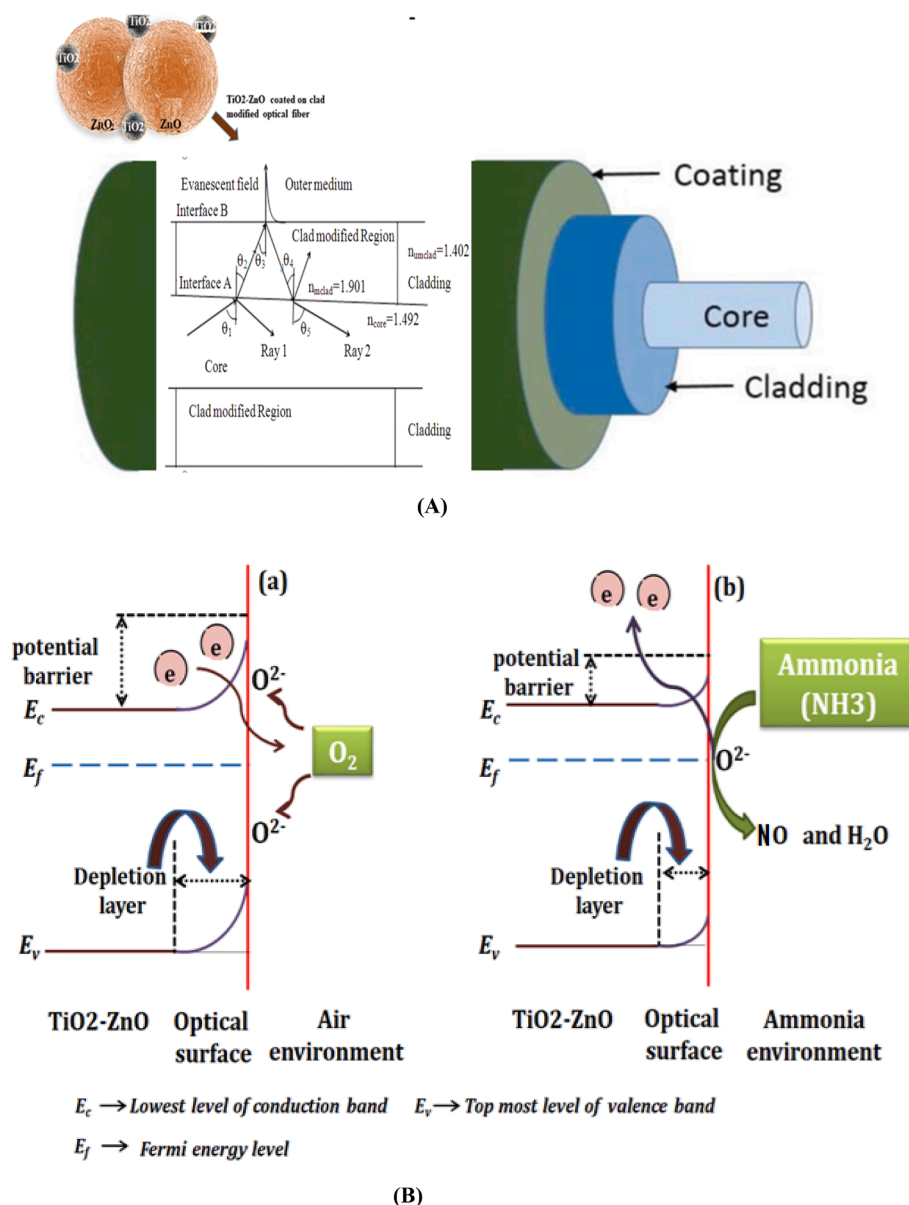


Fig. 7. (A) Gas sensing mechanism in the proposed fiber optic sensor (B) Schematic band diagram of the sensing material in the air and ammonia environment.

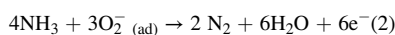
adsorption and desorption of oxygen molecules upon the clad modified region of the PMMA optical fiber. As the S3 annealed sample had a greater sensing response than other samples, we shall examine its mechanism. It was observed that S3 sample calcined at a high temperature of about 1200 °C resulted in larger crystallite size of about 31 nm as observed in XRD and narrowed bandgap, which effects the surface area of the nanocomposite thereby prompting the light to scatter. As annealing temperature increases, bandgap energies have decreased due to reduced interatomic distance and structural modifications. The bandgap energies in the annealing system are significantly influenced by the thermal stresses and the quantum size impact. Reduced bandgap energies at higher annealing temperatures support the growth of grains seen in SEM pictures [23,30]. It is important to note that as surface roughness increases and void-filled grains grow between the grains, porosity rises as well, increasing the material's surface-active area. In the context of the gas sensing properties, this phenomena is significant. Also, doping TiO₂ into ZnO can generate lattice defects and oxygen vacancies in the host structure, causing extrinsic electronic states. The presence of oxygen vacancies as observed in EDS in S3 are also responsible for the enhanced sensing phenomena. The gas adsorption

and reaction processes on the surface of the TiO₂-ZnO composite, which was used in this work, are significantly correlated with the sensor's refractive index.

The TiO₂-ZnO sensor has n type characteristics with refractive index (2–2.7) greater than the PMMA optical fiber, thereby indicating that the spherical TiO₂ that is attached to the ZnO acts as the main charge carrier. With the help of the gas sensing at RT, we can relate the electronic and optical characteristics to the ammonia sensor's gas sensing process. When S3 is exposed to air (in the absence of gas), light enters the clad modified region from the core and returns back through the interface of core-modified cladding (interface A) into the core region, after reflection from the interface of modified cladding-air (interface B) as shown in Fig. 7(A). As the sensor operates in leaky mode condition, the output spectral light intensity of the sensor may result from light travelling through the fiber due to total internal reflection (ray 1) and the back scattered leaky light (ray 2). The intensity of the output spectral light may alter if any modifications are made to these back scattered leaky radiations. In the absence of gas, ambient oxygen adsorbs on the surface of the clad modified S3 region, and takes hold of free electrons that are present in the conduction band of S3 and produce reactive oxygen ions

(O²⁻) [31]. These surface chemical reactions change the optical fiber's refractive index, which regulates how much light is reflected at the air-medium interface due to evanescent wave absorption by the air.

Likewise, when the sensor is exposed to ammonia test gas, the molecules interact with the surface-adsorbed oxygen species thereby undergoing a chemical reaction. This interaction indicates that the evanescent wave absorption disturbs the equilibrium of the applied field to thereby decrease the barrier width as shown in Fig. 7(B). This allows the return of more electrons to the conducting channel, which in turn alters the refractive index and the output spectral response of the sensor. The interaction of oxygen molecules with ammonia vapor is given by the equation



These results presented that the high-temperature annealed TiO₂-ZnO nano-composites can magnificently improve the active adsorption site for ammonia gas sensing at RT.

4. Conclusions

The spectrum properties and changes in peak intensities of a fiber optic sensor using TiO₂-doped ZnO as the cladding material were investigated for various concentrations of acetone, ammonia, and IPA gases. It has been discovered that TiO₂-doped ZnO is a suitable material for detecting VOC toxic gases. Furthermore, when TiO₂ doped ZnO was annealed at 1200 °C, it was revealed that it possessed good gas detection sensitivity for inorganic ammonia at 500 ppm at room temperature and constant relative humidity with a response time of 18 sec. The improved spectral response in the 1200 °C annealed TiO₂-ZnO nanocomposite (S3) likely stems from several factors such as enhanced crystallinity leading to better charge transport, optimal defect concentration providing gas adsorption sites, larger grain size increasing surface area, and favorable material composition promoting gas interaction. As a result, it may be useful for detecting a variety of hazardous gases at room temperature. This work aimed to establish the baseline performance of our TiO₂-doped ZnO material, though further tuning can be done to further use it as a tool in gas sensor applications.

CRedit authorship contribution statement

B. Renganathan: Validation, Methodology. **Manjunath S. Kamath:** Methodology. **M. Silambarasan:** V.K. **Gobinath:** A.R. **Ganesan:** A. **Deepak:** N. **Kannapiran:** K. **Guhan:** Data curation. **Narendhar Chandrasekar:** Formal analysis. **Subha Krishna Rao:** Data curation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Acknowledgements

K.Navaneeth Krishnan and V.C. Pretheesh Kumar helped the FOS parts, one of the authors (B.R.) thanks the DST/SERB in New Delhi, India, for funding assistance under the fast track project for young scientists (Letter No.SB/FTP/ETA-99/2013 dated 03.09.2013 and also to Dr.M.Chidambaram, for financial support.

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