Impact of CeO_2 doped ZnO binary metal oxide nanocomposites as clad modified fiber optic VOC gas sensor for exhaled breath analysis

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Research Article

Keywords: Exhaled breath analysis, Fiber optic sensor, VOCs vapor, CeO2 doped ZnO, morphology, optical property

Posted Date: March 7th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1412923/v1

Abstract

The detection of volatile organic compounds (VOCs) in ambient environments has opened up a new field for the quick, risk-free, and potentially low-cost identification of respiratory illnesses. In this context, CeO_2 doped ZnO nanocomposites were produced through the sol-gel technique at various ratios (CeO_2:ZnO at 1:4, 4:4, and 4:1, respectively), and their gas sensing capability was evaluated and shown using a clad modified fiber optic sensor to study its potential as a VOC detector. The study was based on the concepts of evanescent wave absorption. The modified cladded optical fiber was exposed to the ammonia, ethanol, and methanol gas medium in the testing laboratory. At room/chamber temperatures, the sensor's sensitivity is tested, and was observed that CeO_2 doped ZnO at 4:1 ratio exhibited better sensitivity towards ammonia gas vapour.

1. Introduction

Breath analysis has become one of the most reliable diagnostic procedures available, allowing clinicians to link medical conditions to aberrant quantities of biomarkers in exhaled breath. Based on this context, the detection of VOC has been acknowledged as a new horizon in ailment diagnostic approaches [1,2]. Unambiguously, the release of VOCs such as acetone, ammonia, ethanolamine in the form of human excrements such as sweat, urine, and breath, are un-mistakably linked to various disorders such as diabetes mellitus, renal failure, pulmonary ailments, lung cancer etc as displayed in Fig 1. For instance, Petters discovered the presence of VOC acetone in the exhaled breath of diabetes mellitus patients in 1857, which was theorized later to be related to poor glucose utilization in the blood, leading to greater quantities of acetone emission [1,3]. Likewise, Dent and Walshe reported ethanolamine in the urine of a patient with an amino acid metabolic problem in the liver, which results in primary cancer [4].

Until now, numerous exhaled breath analysis techniques based primarly on chromatographic techniques such as Gas Chromatography (GC), Liquid Chromatography (LC), Mass Spectrometer Chromatography (MSC), Selected ion flow tube mass spectrometer (SIFT-MS) and others have established a promising diagnostic platform. However, owing to their cost, materials, equipment maintenance, and the need for trained staff due to the complexity of operation, they are hard to routinely incorporate in hospitals and clinics as portable real time gas sensors [5]. Metal oxide and rare earth doped based optical fiber sensors may be a viable option for portable real-time exhaled breath analysis, thanks to their small size, portability, low cost, ease of production and operation [6]. In addition, multidisciplinary collaboration between technology developers and clinicians will aid in the development of a commercially viable optical fiber gas sensing technology for exhaled breath analysis that is complimentary to existing traditional procedures with comparable or greater performance. An active sensing material is coupled to a signal transducer at ambient temperature in a conventional fibre optic gas sensor, allowing the sensing material to interact with the VOCs gas vapours [7-15]. As a consequence, a suitable sensing material with a high sensitivity to gases must be chosen and developed. The optical properties of the sensor material, such as absorbance and hence refractive index, evanescent wave,fluctuate, causing the output optical signal to alter [16-23].

ZnO, is perhaps the most studied and prominent binary metal oxides and has a long history owing to its multiethnic disciplines [1,24–27]. However, to enhance its sensing performance, research is being carried out for significant performance at room temperature, tuning its morphology and structure either by doping the binary metal oxide with nobel metals or metal oxides, or synthesizing nanocomposites and so on [27-30]. The current work intends to create various stoichiometric ratios of CeO_2 doped ZnO nanocomposites synthesized via sol-gel route (CeO_2:ZnO at a ratio of 1:4, 4:4, and 4:1, henceforth named as C1Z4, C4Z4, and C4Z1 respectively), that helps to enhance the gas sensing ability at room temperature. Among various dopants, CeO_2 was chosen due to its chemical stability, low redox coupling potential between Ce3+ and Ce4+ ions, simple availability of 4f orbital necessary for oxygen vacancies, and high mobility of oxygen species [1]. To the best of our knowledge, no much reports are available on CeO_2 : ZnO nanocomposite clad modified fiber optic gas sensors to detect VOCs such as ammonia, ethanol and methanol gas vapours for Breath analysis clinically.

2. Experimental Procedure

*2.1.*Synthesis of CeO_2 doped ZnO Nanocomposites and its characterisation

For the synthesis of CeO_2 doped ZnO Nanocomposites as fiber optic gas sensing materials, equimolar ratio (4:4) $Ce(NO_3)_3$ and $Zn(NO_3)_2$ were mixed for 10 min in Deionized water, and the solution was heated and stirred continuously using a magnetic stirrer for nearly one hour until it formed a gel like redox reaction mixture. The mixture was then allowed to slowly settle at the bottom, and then filtered followed by continuous washing with water. The obtained byproduct was sintered overnight to 80°C and was ground to fine powder using mortar and pestle. Finally the powders were calcined again for four hours upto 500°C using a muffle furnace kept at a ramp rate of 5°C/min. The procedure was repeated for the ratio 1:4 and 4:1 $Ce(NO_3)_3$ and $Zn(NO_3)_2$ also as shown in Fig. 2.

The morphology of the as produced C1Z4, C4Z4, and C4Z1 nanocomposites was studied using a Scanning Electron Microscope (JEOL JSM- 6390) operating at a 30 kV accelerating voltage and a High Resolution Transmission Electron Microscope (JEM-2200FS equipment) (JEOL). Energy dispersive spectroscopy (EDS) were utilized to do the elemental analyses (Oxford Instruments, Model No. 7582).

2.2) Fiber optic sensor arrangement for VOC sensing

The systematic fiber optic gas detecting configuration that was put up throughout the experiment is depicted in Fig. 3. This experiment used a tungsten halogen light source with a wavelength range of 100 to 2000 nm and a small fiber optic spectrometer with a spectral range of 100 to 1100 nm. The light source and fiber optic spectrometer, were interconnected via a 30 cm long multimode step index optical fibre (PMMA) with a diameter of 750 m which served as the sensor's heart as mentioned in our previous works [31–33]. To acquire the sensing region, a small portion of the cladding region was carefully etched at the centre of the PMMA fiber to about three centimeters with a blade, such that the core region was not harmed and was then inspected using an optical microscope for its uniformity. Various ratios of CeO_2

doped ZnO sensing materials were then coated upon the etched region via dip coating method and was then allowed to dry at normal temperature. Different concentrations of VOCs gases such as ammonia, ethanol and methanol (0, 10, 20–100 ppm, with an increase of 10 ppm), were prepared and were allowed to pass into the gas chamber to detect its potential as a gas sensing material. The optical absorption measurements were performed upon the sensing materials towards various gases using UV-Vis Spectrometer (Shimadzu, UV-1800) in order to study the absorption effect of the sensing material towards various VOCs.

3. Results And Discussion

*3.1.*Elemental and Structural analysis

A Scanning Electron Microscope (SEM) was utilized to study the morphology of the sensing material. Figure 4(a-c) shows representative SEM micrographs of C1Z4, C4Z4, and C4Z1 nanocomposites having densely agglomerated spherical morphology and their corresponding elements contained in the samples as seen in EDS spectra (Fig. 4(d-f)). Likewise,

Table 1.The At (%) various elements present in C1Z4, C4Z4, and C4Z1 before and after coating upon the optical fiber.

As synthesized CeO_2 doped ZnO	Zn (at.%)	Ce(at.%)	O(at.%)
C1Z4	64.30	16.38	19.12
C4Z4	45.42	31.78.	12.80
C4Z1	17.10	68.35	14.55
Optical fiber coated CeO_2 doped ZnO	Zn (at.%)	Ce(at.%)	O(at.%)
C1Z4	36.72	04.11	30.27
C4Z4	20.42	19.30	30.48
C4Z1	13.83	62.13	18.62

3.2) VOCs Gas sensing Analysis to determine its sensitivity and selectivity

The C1Z4, C4Z4 and C4Z1 samples were evaluated with various concentrations of test VOC gases at low ppm to understand their potential as a breath analyzer, utilising a clad modified optic fibre gas sensor setup, and their individual spectrum responses are shown in Fig. 5. With varying quantities of VOC test gases in 10 ppm increments, the spectral peaks were observed at 670, 757 and 935 nm wavelengths. All the gases displayed spectral peaks at these wavelengths, however their intensities differed in incremental and decremental orders. The spectral response peaks clearly depicted that the sensor's consistency with ammonia was better compared to other VOC test gases at room temperature.

Further, the gas sensitivity was measured for all the samples by plotting a graph with intensity along y-axis and concentration of various ppm's of VOC test vapours of ammonia, ethanol and methanol along the x-axis for the spectral points at 690 nm as shown in Fig. 5. An encompassed Table has been presented to display the gas sensitivity of the samples in the presence of various test gases as shown in Table 2. The gas sensitivity was observed to be the highest for C4Z1 sample with a negative slope observed as -2.6 counts/10 ppm for ammonia, compared to other test gas vapours;

the negative sign indicating the larger leakage of light. Figures 6(a-i) give the plot between the spectral peak intensity gases ammonia,ethanol and methanol at 690 nm, 757 nm and 935 nm.. The results show that CeO_2 doped ZnO is highly selective to ammonia as for other gases the sensitivity is very less. (Table.2)

Table 2
Gas sensitivity along with increase and decrease in spectral intensity of various samples towards the test gases at room temperature.

Test Gas Vapours	Gas Sensitivity (10 counts/ppm)											
	C4Z1				C4Z4				C1Z4			
Ammonia	2.6	2.0	0.7	↓	1.3	1.0	0.8	↑	1.4	1.1	0.6	↓
Ethanol	1.6	0.9	0.3	↑	1.4	1.2	0.2	↑	0.7	0.5	0.3	↓
Methanol	1.7	1.4	1.3	↑	2.1	1.8	0.9	↓	1.0	0.8	0.7	↓

A bar diagrammatic representation of the gas sensitivity is displayed in Fig. 7(a) for various test gases at maximum spectral peak intensities 690 nm, 757 nm and 935 nm respectively. Interestingly, C4Z1 showed decrease in the magnitudes of spectral intensities from its reference value (0 ppm), which is due to more evanescent light absorption at the boundary between C4Z1 and the test gas ammonia, resulting in changes in its refractive index. Rare earth CeO_2 helped in enhancing the gas sensing ability of ZnO for C4Z1, as the concentration of CeO_2 was larger than ZnO. As ZnO is a wide band gap semiconductor, inclusion of more concentration of dopant RE state of CeO_2 into host ZnO, narrowed the Fermi energy level and reduced the band gap between the valence and conduction band, thus enhancing better conduction mechanism. Upon bonding, every rare earth CeO_2 loses its electrons, and thus the 4f electrons occupy gradually the majority spin states thereby increasing the total magnetic moments and its conduction state. Likewise, the sensitivity percentage was calculated for C4Z1 sample towards the low concentrations (0-100 ppm) of test gas ammonia and the sensitivity (%) was observed to be 12.5% at the maximum of 100 ppm as shown in Fig. 7(b).

The sensitivity (%) was calculated using the formula $((I-I_0)/ I_0)* 100$ wherein the maximum spectral peak intensity of ammonia at 100 ppm (denoted as I) was subtracted with the maximum spectral peak intensity of reference (0 ppm) (denoted as I_0).

3.3 UV absorption spectra

The C4Z1 sample was studied using UV–Vis Absorption Spectroscopy since it had a greater sensing response than the other samples. Optical analysis was performed to determine the absorption capability of the material in various test gas conditions. UV–Vis absorption spectroscopy was performed by depositing the sample on one of the cuvette's inner walls and pouring 1 ml of the solution (ethanol, methanol, and ammonia) into its bottom at a time to generate vapour [34]. A comparable cuvette was used to capture the same quantity of fluid without the sample coating for comparison, and the spectra were recorded.

Fig. 8 depicts variations in the UV–Vis absorption spectra for C4Z1 in the presence of air, ethanol, and ammonia gas environments, with visible light wavelengths ranging from 300 nm to 400 nm. In the case of ammonia, absorbance increases as the wavelength increases, however in the case of air and ethanol, absorbance decreases. C4Z1 had a high interaction, which can be ascribed to its smaller particle size, which affects its surface to volume ratio, enhancing absorption.

4. Conclusion

Prior to gas testing, we used SEM, EDS, and HRTEM methods to validate the shape and composition of rare earth CeO_2 doped ZnO nanocomposites manufactured through the sol gel process for varied stoichiometric ratios. A clad modified fiber optic gas sensor covered with CeO_2 doped ZnO was utilized to detect VOCs such as ammonia, ethanol, and methanol gases for low concentrations at ambient temperature (0-100 ppm, with step increment of 10 ppm).

When compared to ethanol and methanol vapours, the CeO_2 doped ZnO (4:1) sensor was particularly sensitive to ammonia, with a sensitivity of around 2.6 counts/10 ppm for ammonia and a sensitivity (percent) of 12.6 percent at 100 ppm.

Declarations

Acknowledgement

Dr.S.M.M.S.Maricar and Mr.Noble assisted with characterization and experiments, and one of the authors (B.R.) acknowledges the DST/SERB in New Delhi, India for financial support through the fast track project for young scientists (Letter No.SB/FTP/ETA-99/2013 dated 03.09.2013).

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Figures

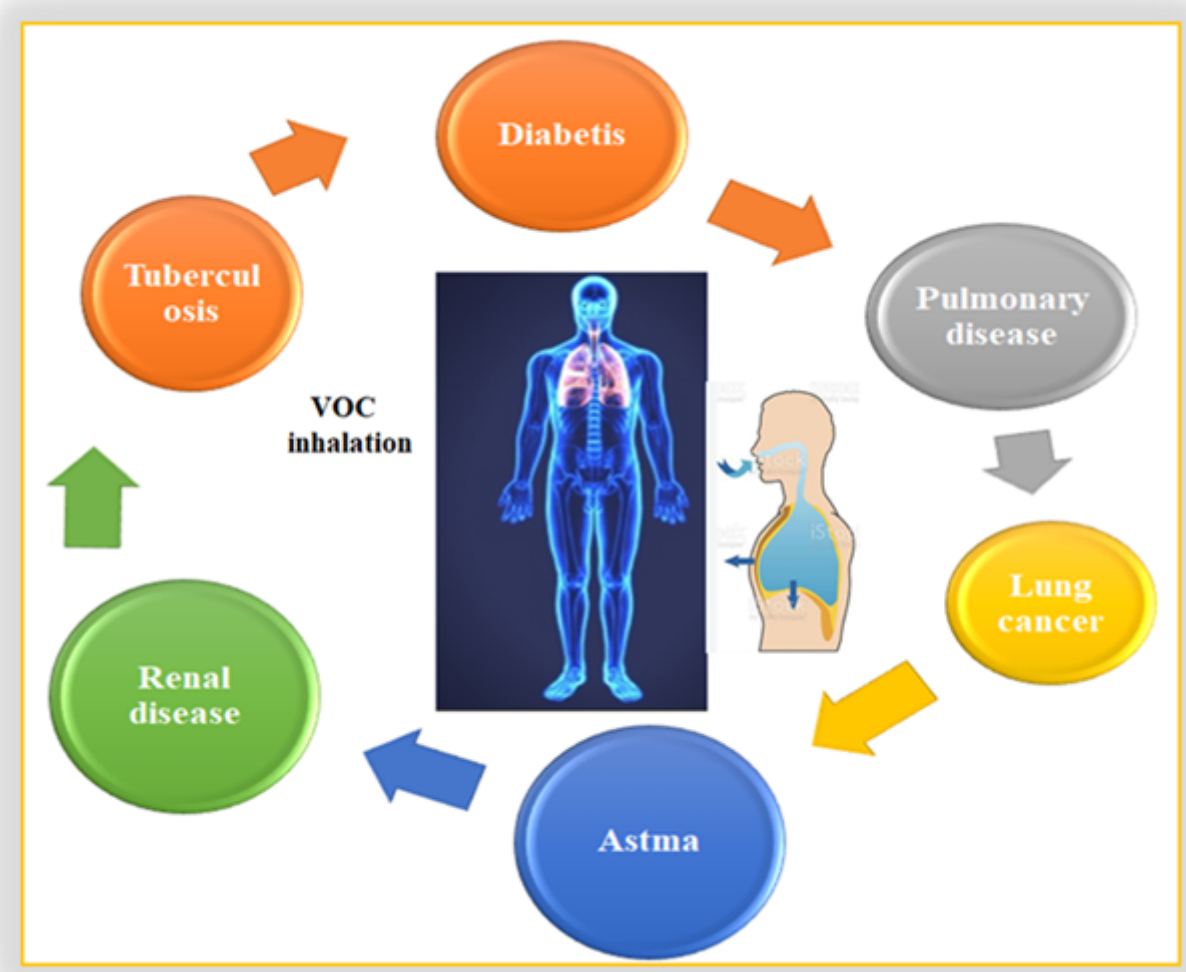

Figure 1

Various health disorders due to Volatile organic compounds inhalation.

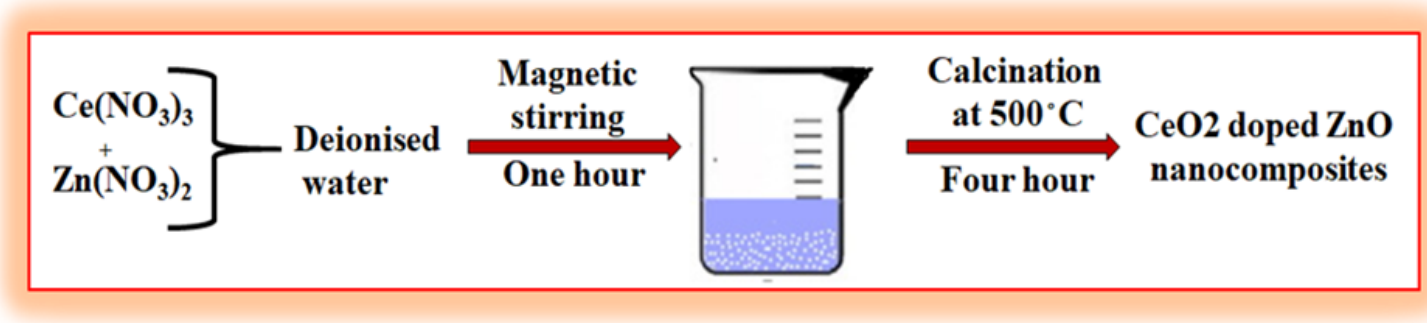

Figure 2

Schematic representation for the synthesis of CeO2 doped ZnO nanocomposites .

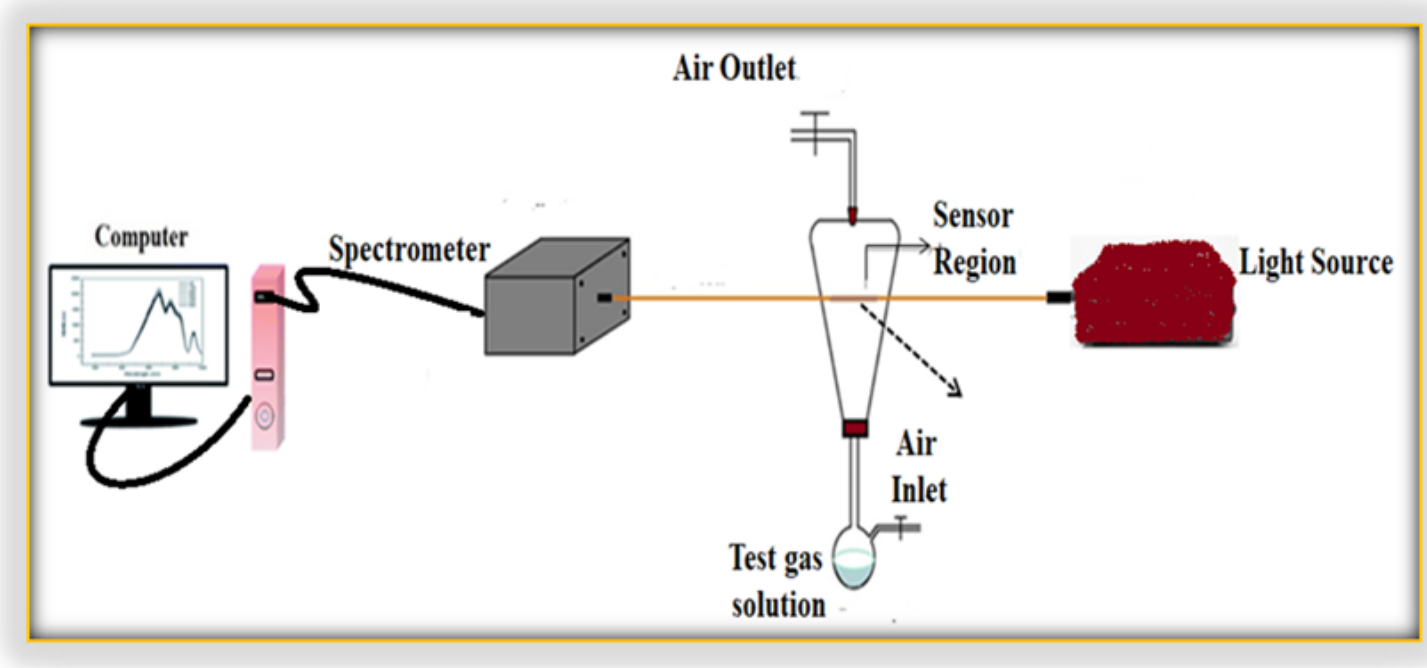

Figure 3

Schematic Fiber optic gas sensing set up.

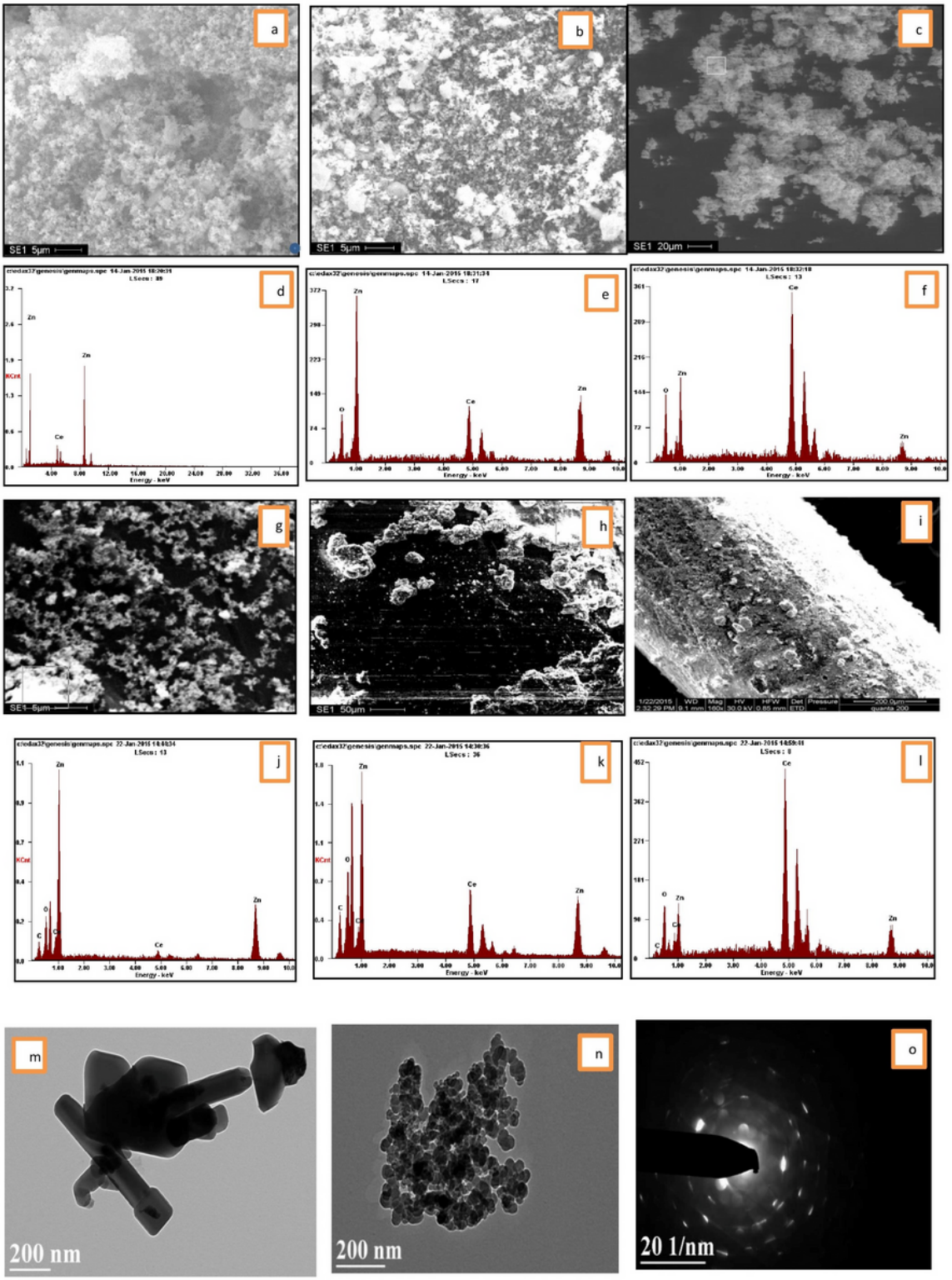

Figure 4

(a-f) SEM images and EDS spectrum of C1Z4, C4Z4, and C4Z1, Fig. 4(g-l), Fiber coated SEM and EDS spectrum of C1Z4, C4Z4, and C4Z1 samples, and (m-o) HRTEM images of C4Z1 sample.

(g-i) displays the SEM images of optical fiber coating C1Z4, C4Z4, and C4Z1 sensing materials with their respective EDS in Fig. 4(j-l). TEM analysis was performed upon C4Z1 sample and it clearly displayed

nanorod like structures that are densely agglomerated with its respective[35], SAED pattern (Fig. 4(m-o)). The Table 1, represents the atomic (%) of Zn, Ce and O in various ratios of composites formed before and after coating on the optical fiber.

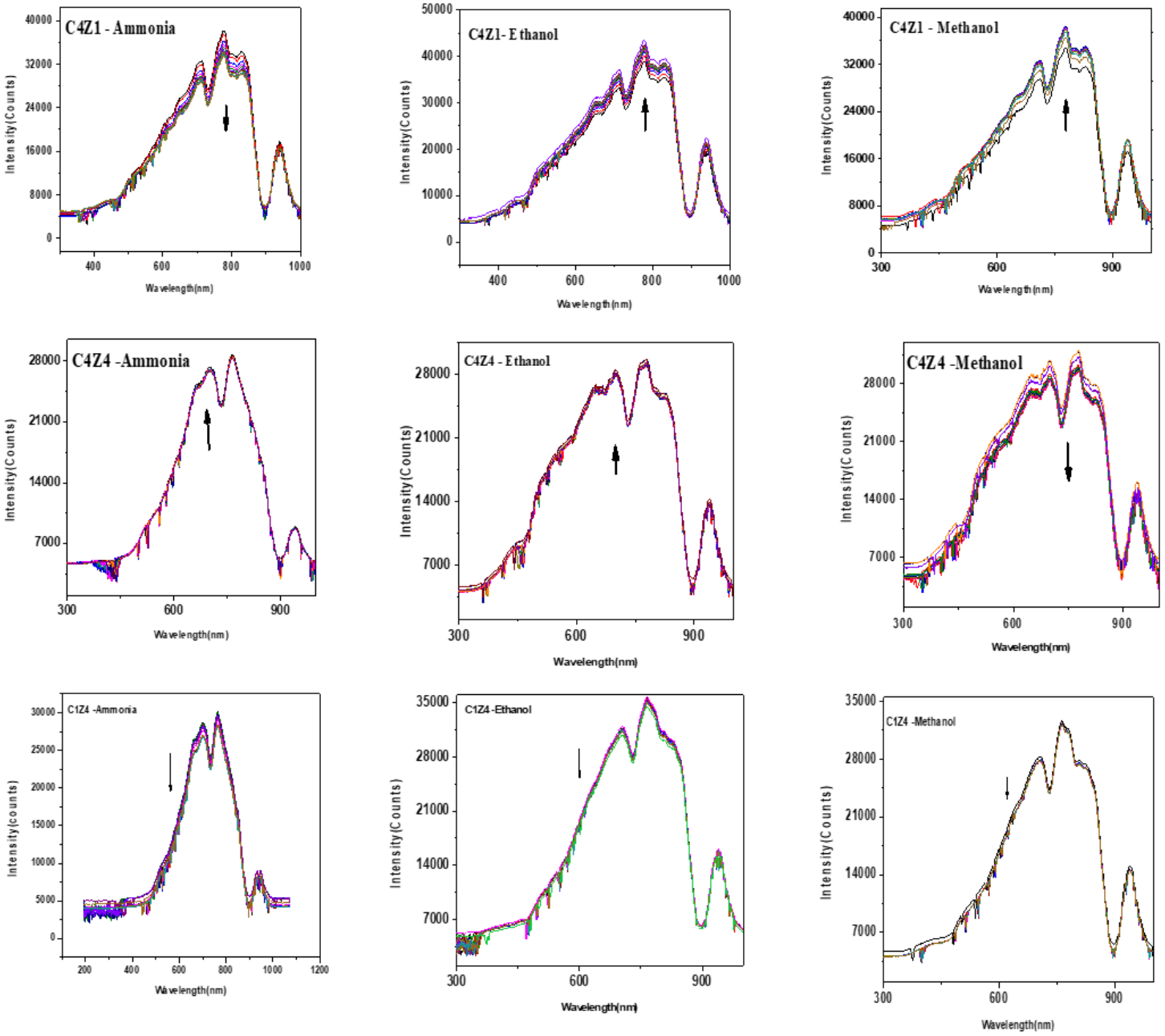

Figure 5

(a-i) Spectral response CeO_2 doped ZnO for ammonia , ethanol and methanol.

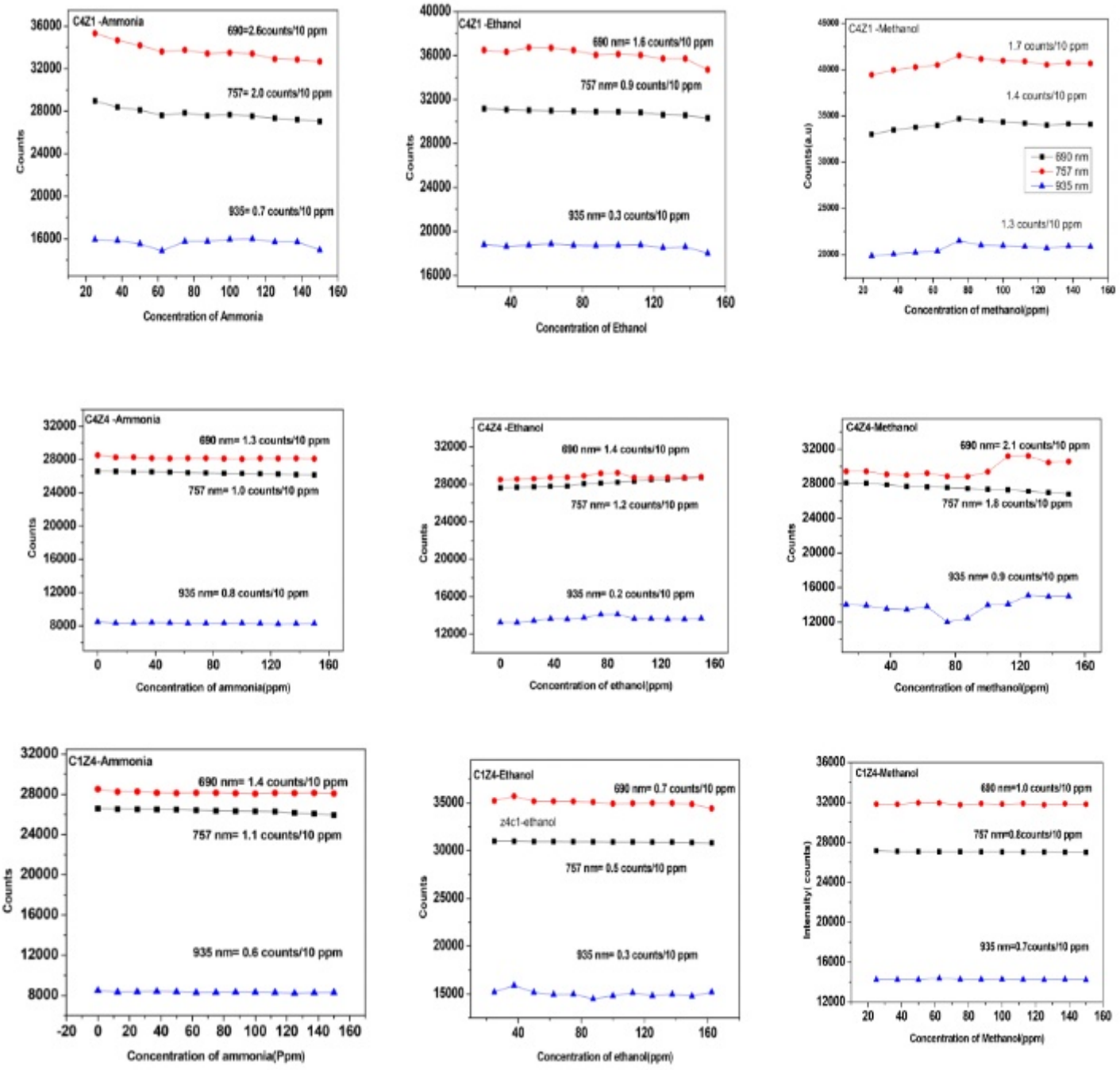

Figure 6

Gas sensitivity of the synthesized samples towards various test gases ammonia , ethanol and methanol at 690 nm, 757 nm and 935 nm.

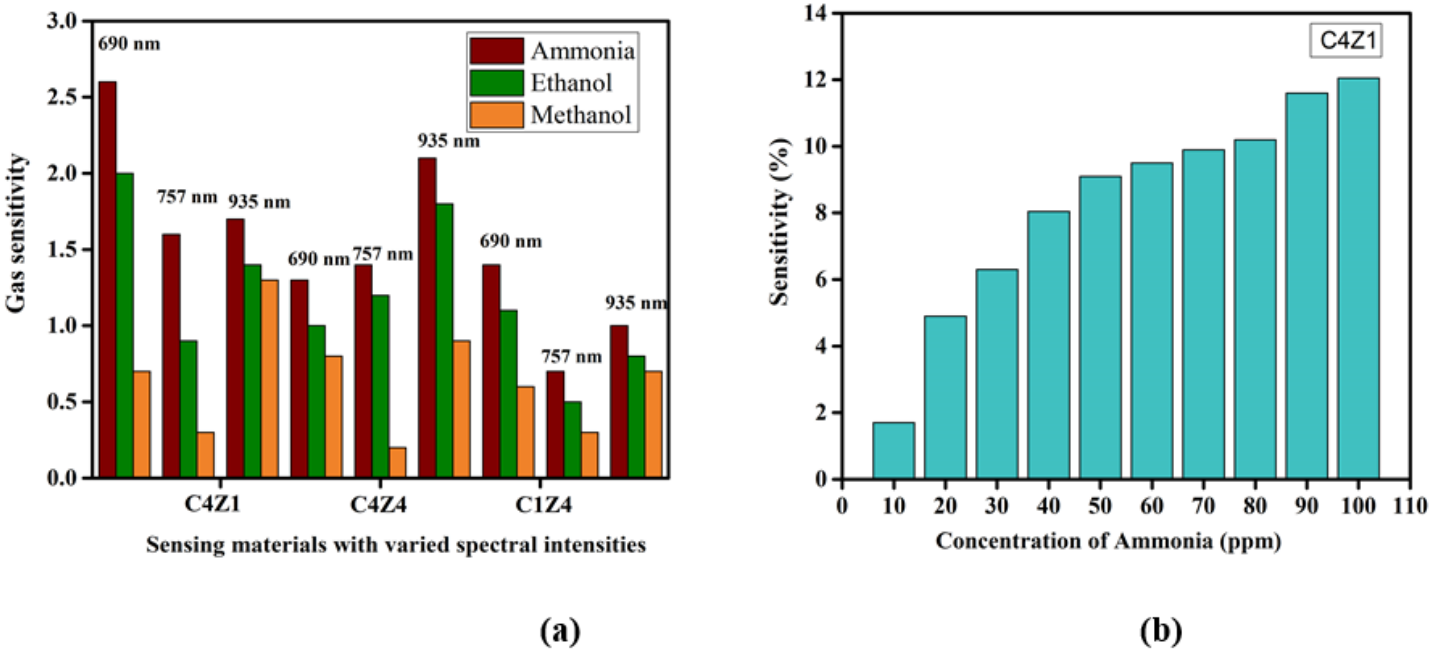

Figure 7

(a) Bar diagramic representation of the gas selectivity of various samples towards test gases Ammonia, Ethanol and Methanol at peak intensities 690 nm, 757 nm and 935 nm. (b) Sensitivity (%) of C4Z1 sample towards various concentrations of ammonia test gas.

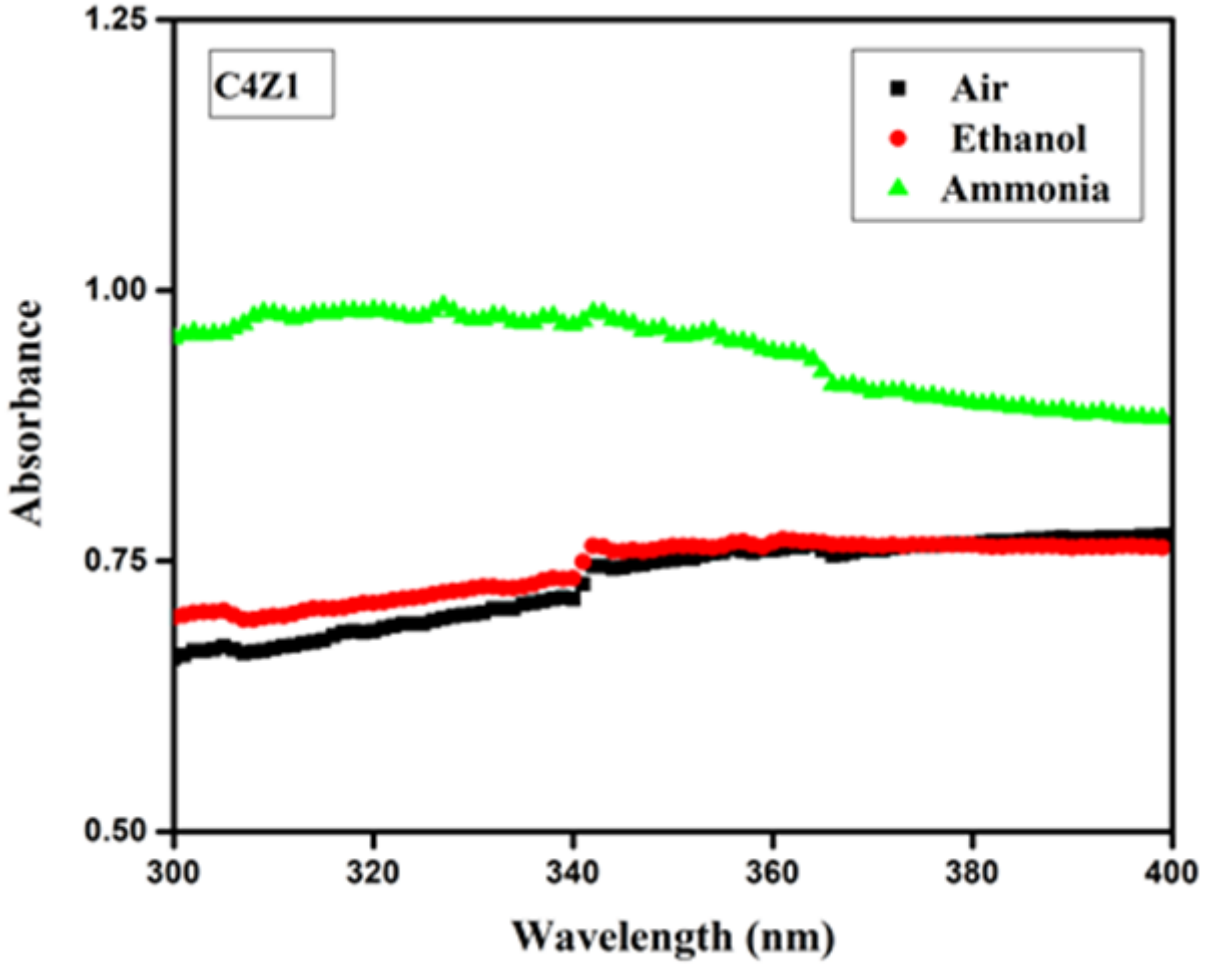

Figure 8

Absorption spectra of C4Z1 in air, ammonia and ethanol test gas environments.