

RESEARCH

On the Improvement of Ethanol Sensing by Co₃O₄ Loaded SnO₂ Nanoparticles

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ABSTRACT

Undoped and Co₃O₄-loaded (5, 10, and 15 at.%) SnO₂ nanoparticles were prepared by a simple co-precipitation method. X-ray diffraction (XRD) study confirmed the presence of tetragonal phase of SnO₂ and cubic stage of Co₃O₄ in accumulation to this the preferred orientation and texture coefficient were derived. The texture coefficient of (200) plane increases with parallel decrease in (110) plane, which indicate the development of voids like vacancies along (110) direction. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) analyses recognized the uniform dispersion of spherical shaped nanoparticles. EDS analysis confirmed the impurity absence in the prepared samples. UV-Vis absorption analysis confirmed that the optical band gap will get red shifted from bulk which is due to the agglomeration of nanoparticles and also due to the influences of Co₃O₄. The absorption peaks broadens after loading Co₃O₄ which indicate the surface related defects in the samples. The refractive indices derived from the band gap values had confirmed the fiber-optic sensor working under the leaky mode operation. Vibrating sample magnetometer (VSM) results confirmed the behavior of ferromagnet in pure SnO₂ and antiferromagnet stage in Co₃O₄ loaded SnO₂. The undoped SnO₂ with room temperature ferromagnetism (RTFM) shows better sensitivity. The sensitivity of SnO₂ and Co₃O₄ loaded SnO₂ samples were 0.076 and 0.084, respectively. The enhanced sensitivity of Co₃O₄ loaded SnO₂ was due to the high catalytic activity of Co₃O₄.

KEYWORDS

Nanoparticles, texture coefficient, fiber-optic sensor, ferromagnetism.

INTRODUCTION

Oxide heteronanostructures offer remarkable physicochemical properties for the uses of photocatalysts, photovoltaic gadgets, and sensors because of a synergistic mix of different materials [1-3]. Tin dioxide (SnO₂), is a chief n-type semiconductor with wide band gap energy ($E_g=3.6$ eV). Furthermore, it is widely recognised for its potential technological uses in solar cells, transistors, gas sensors, transparent conducting electrodes, and energy storage systems such as lithium batteries [4-7]. The primary applications of SnO₂-based nanoparticles have been in gas detection, along with great chemical stability, notable selectivity, and quick response times. Numerous factors

affect the sensors' sensitivity and selectivity, but the most significant ones are the foreign modifiers scattered over the semiconducting oxides. As typical such foreign modifiers are well known noble metals like Pd and Pt, which are used in a practical device [8,9]. The results are associated with the high activity of noble metals for the catalytic oxidation of reducing gases; Ag, Au, or CuO, as well as Co₃O₄, have also been found to have comparable results [10-13]. These examples demonstrate the complete link between catalytic and gas sensing abilities. The sensitizing properties of transition metal oxides, which are frequently employed as catalysts for the oxidation of reducing gases like Co₃O₄ and CuO, are therefore of significant interest. Co₃O₄, a distinctive p-type semiconductor with a narrow band gap

($E_g=1.4$ eV) is generally used in catalysts and gas sensors [14]. Jeong *et. al.* prepared $\text{Co}_3\text{O}_4/\text{SnO}_2$ core shell hollow spheres by galvanic substitution, and the creation of nanoscale p-n junctions and Co_3O_4 catalytic activity was credited with the increased sensor responsiveness. Bekermann *et. al.* [15] reported that the reduced particle size, formation of p-n junction and catalytic activity of Co_3O_4 enhance the gas sensing characteristics of $\text{ZnO}/\text{Co}_3\text{O}_4$ nanocomposite. Decorating n-type ZnO nanowires with p-type nanoclusters like NiO , Mn_3O_4 , and Cr_2O_3 can greatly improve the gas responses of ZnO nanowire networks [16-18]. A drop in hole concentration caused the electron depletion layers in ZnO nanowires beneath the p-type nanoclusters to extend radially, which increased the gas responses. Wang *et. al.* [19] investigated $\text{Co}_3\text{O}_4/\text{SnO}_2$ gas sensors using NH_3 and $\text{C}_2\text{H}_5\text{OH}$ as a target gas at an operating temperature of 200 and 240 °C, respectively. The improvement in sensing behavior was due to core-shell nanostructure and the synergetic effect between Co_3O_4 and SnO_2 . According to Zhang *et. al.* [20], the expansion of the space charge layer caused by the distinct work functions of the Co_3O_4 and SnO_2 metal oxides alters conduction when exposed to the target gas. In addition to this both SnO_2 and Co_3O_4 exhibit RTFM due to strong exchange interactions of the singly charged oxygen vacancies of the defective semiconductor powders [21,22]. Even though reports on $\text{Co}_3\text{O}_4/\text{SnO}_2$ based ethanol sensor are available, reports on ethanol sensing of $\text{Co}_3\text{O}_4/\text{SnO}_2$ using fiber-optic sensor at room temperature (RT) are not found in elsewhere in the literature. Hence in this work Co_3O_4 loaded SnO_2 nanoparticles have been synthesized and both magnetism and sensitivity towards ethanol gas are studied at room temperature.

EXPERIMENTAL

Synthesis of Co_3O_4 loaded SnO_2 nanoparticles

Pure and the Co_3O_4 loaded (5, 10, 15 at.%) SnO_2 nanoparticles were prepared by the simple co-precipitation method [20,23]. A typical synthesis involves dissolving tin (IV) chloride (SnCl_4) (0.1 M) in 250 ml of distilled water, stirring the mixture magnetically, and adding drops of aqueous ammonia solution to keep the pH of the mixture at 7. At last, the final solution was continuously stirred for a duration of one hour. After a centrifugation, the precipitate was repeatedly cleaned with ethanol and distilled water. To obtain SnO_2 nanoparticles, it is dried in air at 60 °C to eliminate the chloride and other unreacted ions. Co_3O_4 loaded (5, 10, 15 at.%) SnO_2 nanoparticles are achieved by adding the appropriate amount of Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) to the SnO_2 stock of solution. The resulting nanoparticles were then annealed for two hours in air at 600 °C. The prepared samples were labeled as S0, S5, S10, S15 for pure and Co_3O_4 loaded (5, 10, 15 at.%) nanoparticles, respectively.

Characterization

The X-ray diffraction (XRD) of undoped and Co_3O_4 -loaded SnO_2 nanoparticles was conducted at room temperature (RT) using a PANalytical X'Pert X-ray diffractometer. The $\text{Cu-K}\alpha$ radiation (wavelength: 1.54056 Å) was used, with a step size of 0.02° and a 2D range of 10° to 90°. The high-resolution transmission electron microscope (HRTEM) (PHILIPS, model CM200) with an accelerating voltage of 200 kV, the energy dispersive X-ray spectroscopy (BRUKER) operating at a voltage of 30 kV, and the scanning electron microscope (SEM, VEGA 3 TESCAN) were used to analyze the morphology, size distribution, and elemental composition of the samples. The UV-Vis absorption spectrometer (Shimadzu-2450) was used to record the UV-Vis absorption spectra at RT. FTIR (Fourier transform infrared) spectra were measured by using the KBr method on a Fourier transform infrared spectrometer (Shiraz) at RT in the range of 4000 – 400 cm^{-1} and with a resolution of 1 cm^{-1} . The magnetic measurements were carried out using vibrating sample magnetometer (VSM) and the ethanol sensitivity was measured using fiber-optic sensor.

RESULTS AND DISCUSSION

X-Ray diffraction analysis

The XRD pattern of Co_3O_4 loaded SnO_2 nanocomposites are shown in the Fig. 1. All the diffraction peaks for the S0 corresponds to a tetragonal phase of SnO_2 . These patterns are in an agreement with the Joint Committee on Powder Diffraction Standards (JCPDS). For S5, S10, and S15 along with the SnO_2 peaks one extra peak is observed at 2θ of 31.36°, which can be indexed to a plane (220) of cubic Co_3O_4 . As the quantity of cobalt oxides increases, the diffraction peaks broaden, indicating that the processed samples have decreasing crystallite sizes. The crystallite size and lattice properties of SnO_2 have been determined using Scherrer's equation and are shown in Table 1. Furthermore, the texture coefficient (TC) can be used to determine the preferred orientation of SnO_2 . Thus TC has been calculated by using the following formula,

$$TC_{hkl} = \frac{I_{(hkl)} / I_{0(hkl)}}{(1/N) \left[\sum_N I_{(hkl)} / I_{0(hkl)} \right]}$$

where N is the number of diffraction peaks taken into consideration, $I_{(hkl)}$ is the measured intensity, and $I_{0(hkl)}$ is the relative intensity of the corresponding hkl plane supplied in JCPDS. $TC_{(hkl)}$ is the texture coefficient of the hkl plane [24]. The major XRD peaks are associated with diffraction peaks of (110), (101), (200), and (211) planes and their intensities are varied for samples loaded with different amount of Co_3O_4 . The Texture coefficient for these planes are calculated and tabulated in Table 2.

Nanoparticles with randomly oriented crystallite have a $T_c \approx 1$; on the other hand, a given (hkl) direction has an abundance of grain when $T_c > 1$, and lack of grain when $T_c < 1$. The TC values indicates that only (110) and (200) planes have greater than one TC. Nevertheless, when Co_3O_4 is added to SnO_2 , the TC of the (200) plane rises while the (110) plane concurrently decreases. This causes a drop in the planar density of the (110) plane when Co_3O_4 is loaded. According to the texture coefficient, the (110) planar density drops as the (200) planar density increases, reaching a maximum for the S15 sample. The S15 sample's numerous voids are confirmed to be located on the (110) plane by this result. The effect of these changes on gas sensing properties has been discussed at the sensing analysis section.

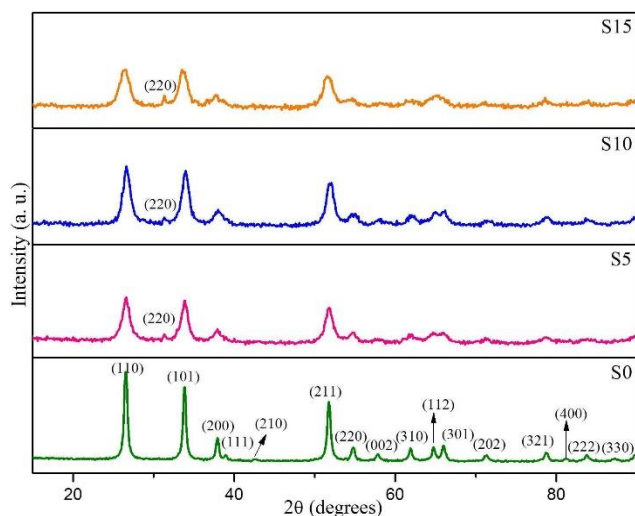


Fig. 1. XRD pattern of pure and Co_3O_4 loaded SnO_2 nanoparticles.

Table 1. Lattice constant and crystallite size of Co_3O_4 loaded SnO_2 nanoparticles.

Samples	Lattice constant (Å)		Crystallite size D (nm)
	a	c	
S0	4.7378(1)	3.1833(1)	16
S5	4.7311(1)	3.1910(1)	8
S10	4.7331(1)	3.1854(1)	7
S15	4.7440(1)	3.1775(1)	6

Table 2. Texture coefficient for different planes.

Samples	$T_{c(110)}$	$T_{c(101)}$	$T_{c(200)}$	$T_{c(211)}$
S0	1.058	0.929	1.158	0.853
S5	1.046	0.874	1.352	0.710
S10	1.029	0.887	1.368	0.730
S15	1.011	0.819	1.533	0.635

SEM with EDS analysis

The SEM micrograph of S0 and S15 samples as shown in Fig. 2 and EDS spectra of the samples are shown in Fig. 3. The SEM image makes it evident that the generated

samples are in the nano range and have a nearly uniform structure. Nanoparticles that have been aggregated make up the images. The significant concentration of OH⁻ ions in the samples has been predicted to cause this aggregation in the wet chemically produced nanoparticles [25]. EDS was performed to confirm the further composition of the as-prepared products. The spectra make it evident that, in pure SnO_2 , only the peaks corresponding to Sn and O have been found; in samples of SnO_2 loaded with Co_3O_4 , cobalt peaks have also been discovered. These measurements exclude the presence of any impurity elements in the samples.

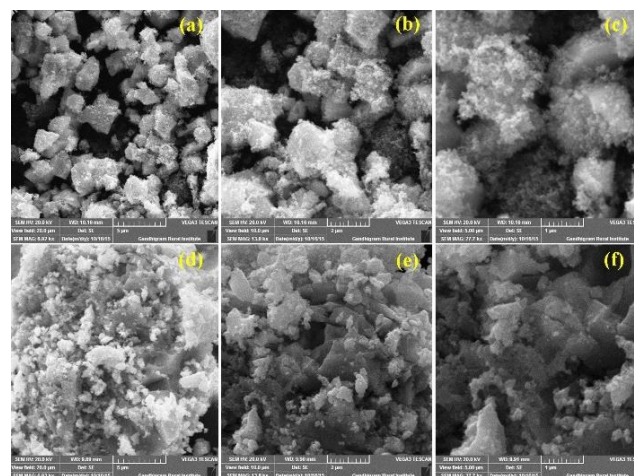


Fig. 2 SEM images of (a-c) S0, (d-f) S15 samples

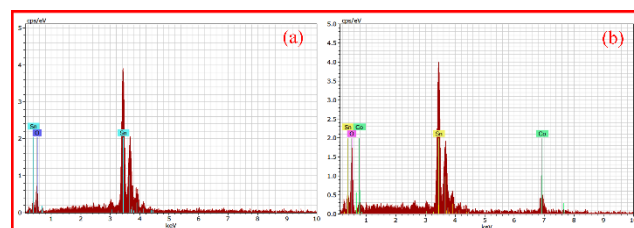


Fig. 3 EDS spectra of (a) S0, (b) S15 samples

HRTEM analysis

TEM studies were conducted on a pure SnO_2 sample, shown in Fig. 4, to determine the size and morphology of the nanoparticles. The picture illustrates the spherically shaped nanoparticles that have been seen to aggregate. The diameters of the nanoparticles are between 8 and 15 nm, which is consistent with the findings from the XRD analysis. The high resolution image given in Fig. 4(d) and Fig. 4(e) revealed the presence of particle having 11 nm size with the lattice spacing of 1.66 Å corresponding to the (220) plane of tetragonal rings. The selected area electron diffraction (SAED) pattern of SnO_2 nanoparticles is shown in Fig. 4(f), where the polycrystalline nature of the nanoparticles is shown by the concentric rings. These diffraction rings align with the XRD peaks of SnO_2 and are indexed to the (110), (200), (111), (220), and (311) planes of the tetragonal-phase.

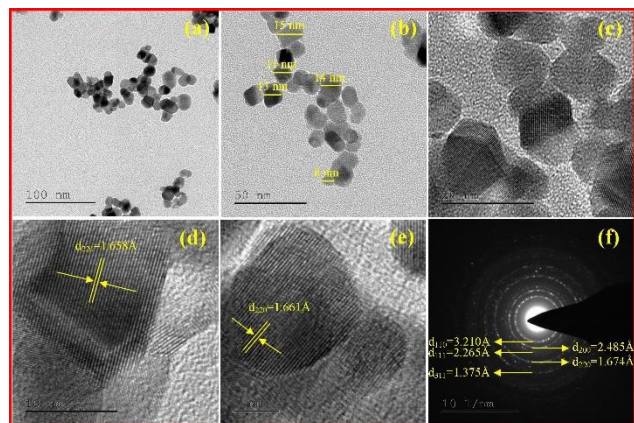


Fig. 4. (a -c) TEM images, (d and e) HRTEM images, (f) SAED pattern of SnO₂ nanoparticles.

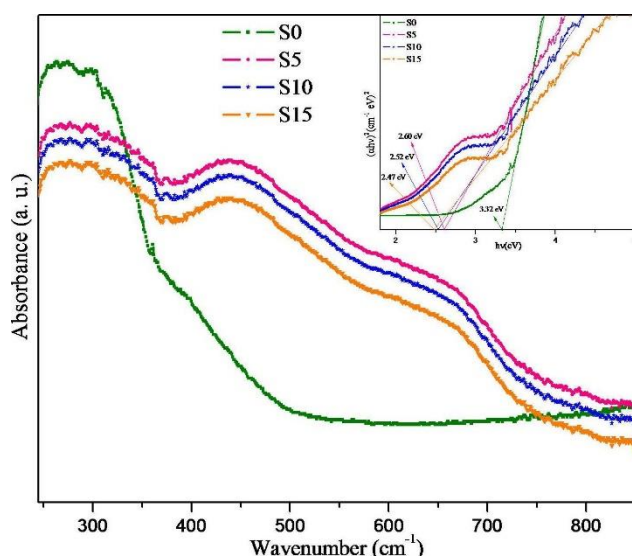


Fig. 5. UV-Vis absorption spectra of pure and Co₃O₄ loaded SnO₂ nanoparticles.

UV-Vis analysis

Fig. 5 shows the optical absorption spectra of pure and Co₃O₄ loaded SnO₂ nanoparticles. High transparency in the visible range and substantial UV absorption are displayed by pure SnO₂. As a result of surface-related defects being created during the composite's production, the spectra displayed a broad absorption [26]. The absorption in the visible region attributed to the presence of Co₃O₄ phase. The O²⁻ → Co²⁺ charge transfer process, or valence to conduction band excitation, is associated with the first absorption band in the visible area, whereas the O²⁻ → Co³⁺ charge transfer, or the Co³⁺ level below the conduction band, is associated with the second band [27]. The inset of Figure 5 displays the α -absorption plot, which is used to determine the optical band gaps of the samples. The aggregation of nanoparticles causes the band gap for pure SnO₂ to redshift from 3.60 eV to 3.32 eV. When comparing the band gap of Co₃O₄ loaded SnO₂ nanoparticles to that of

pure SnO₂, a red shift is seen. Co₃O₄ 1.4 eV band gap is the cause of this shift in energy toward lower values in Co₃O₄ loaded SnO₂ samples. Ultimately, the samples' refractive indices are determined using the Moss relation, and for the S0, S5, S10, and S15 samples, respectively, they are 2.312, 2.458, 2.477, and 2.490. These refractive index values are higher than those of the fiber's core and cladding. Because of this, the fiber-optic sensor that uses these samples as sensing materials operates in a leaky mode.

FTIR analysis

The FTIR spectra of pure and Co₃O₄-loaded SnO₂ nanoparticles are displayed in **Fig. 6**. The hydroxyl group's O-H stretching vibration is represented by the peak at 3420 cm⁻¹, whereas the physisorbed water molecules' H-O-H bending vibration mode is at 1623 cm⁻¹ on the sample's surface [28]. Vibration mode observed at 2916 cm⁻¹ is due to C-H stretching vibration. The band at 2372 cm⁻¹ confirmed the presence of CO₂ molecule, which could be observed since the measurement is taken in air. The peak at 1400 cm⁻¹ is assigned to the symmetric stretching of the carboxyl group, C=O and 1029 cm⁻¹ is associated with the C-O-C vibration. The band observed at 513 and 631 cm⁻¹ are assigned to stretching vibration of Sn-O and O-Sn-O, respectively [29]. The presence of the spinel structure of Co₃O₄ in the Co₃O₄ loaded SnO₂ is confirmed by the observation of two additional absorption bands at 664 and 560 cm⁻¹ for S15, which are the result of the metal-oxygen bond's stretching vibrations. The OB₃ vibration in the spinel lattice is associated with the first band, while the ABO₃ vibration is associated with the second band. A and B stand for Co²⁺ (3d⁷) in a tetrahedral hole and Co³⁺ (3d⁶) in an octahedral hole, respectively.

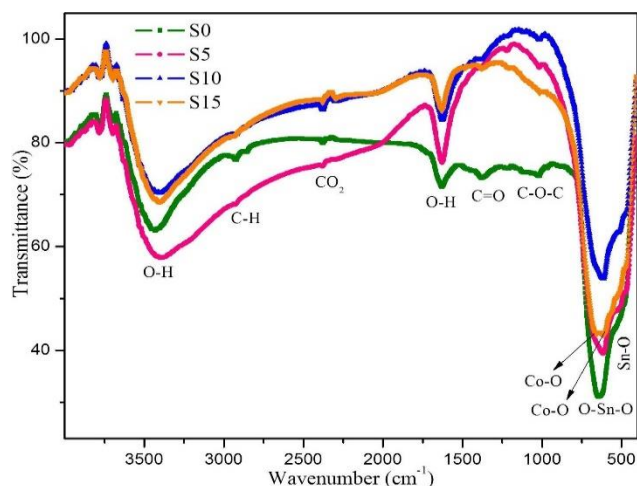


Fig. 6. FTIR spectra of pure and Co₃O₄ loaded SnO₂ nanoparticles.

VSM analysis

Using VSM, the magnetic characteristics of both pure and Co₃O₄-loaded SnO₂ nanoparticles were examined. M(H) measurements is carried out for the magnetic field of -5

$\text{KOe} \leq H \leq +5 \text{ KOe}$. **Fig. 7** depicts the M-H curves measured on S0, S5 and S15 at 300 K. S0 sample shows hysteresis at room temperature, corresponding to the ferromagnetic behavior. The ferromagnetism in S0 is due to the uncompensated spins on the surface of the nanoparticles. The uncompensated surface spins originate from the surface of the nanoparticles is due to oxygen vacancies [30,31]. As the grain size is smaller the surface to volume ratio is higher will result in many more surface vacancies. The S5 and S15 samples show hysteresis at low field region only which can be seen from the inset of **Fig. 7**. The hysteresis in S5 and S15 does not show any tendency to saturate even at high magnetic field of 5 Koe. This is consistent with the observation that it is challenging to achieve saturation of magnetization for nanoparticles due to the presence of broken exchange bonds and surface canted spins. However, the small coercivity value suggests the presence of weak magnetic interactions, which result from interactions between uncompensated spins on the surface. The linear shape of the M-H curve at higher magnetic fields represents the characteristic feature of the antiferromagnetic behavior of the sample [32,33]. The M-H curve of S5 and S15 indicates the presence of antiferromagnetic component along with the ferromagnetic phase. The magnetization gets enhanced in S5 and S15, when compared with S0, but the unsaturation in S5 and S15 is due to antiferromagnetic nature of Co_3O_4 [34,35].

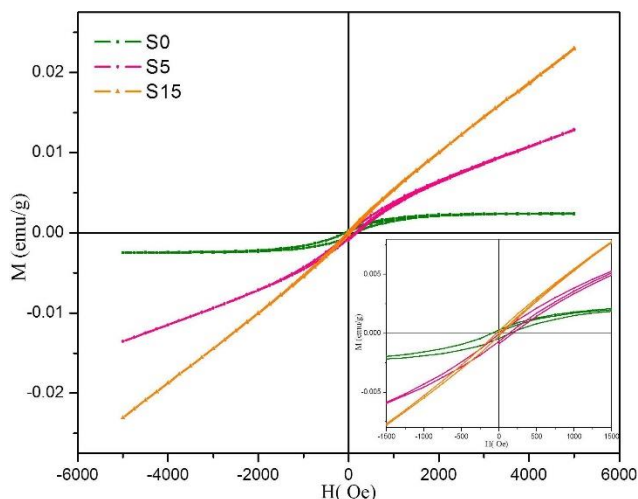


Fig. 7. VSM spectra of Pure and Co_3O_4 loaded SnO_2 nanoparticles. Inset shows the magnification of central part of M(H) curve.

Ethanol sensing properties

The clad modified fiber optic approach was used at RT to study the ethanol sensing properties of S0 and S15. **Fig. 8** and **Fig. 9** depict, respectively, the spectrum response of S0 and S15 nanoparticles to varying ethanol concentrations ranging from 0-500 ppm. Three distinct peaks can be seen in the spectra at 677, 761, and 936 nm. For S0 and S15, the intensity of the spectra increases as the ethanol concentration rises and drops as the ethanol concentration

falls. Therefore, for S15, ethanol absorbs more evanescent field than air. Since the spectral peaks at 677 nm show greater change with ethanol gas concentration, the sensitivity was calculated using the intensities at this wavelength.

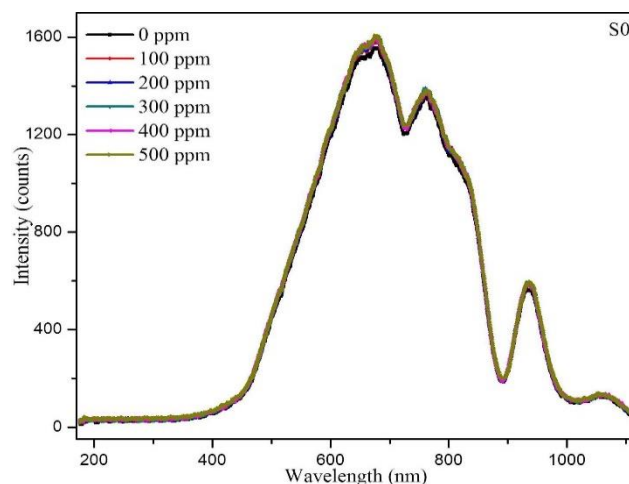


Fig. 8. Spectral response of S0 toward various (0-500 ppm) ethanol concentrations.

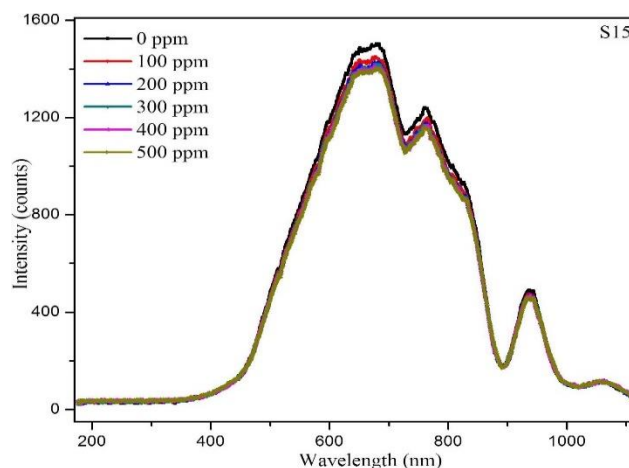


Fig. 9. Spectral response of S15 toward various (0-500 ppm) ethanol concentrations.

Gas sensing characteristics for pure and Co_3O_4 loaded SnO_2 nanoparticles

Fig. 10 presents the variation in the sensitivity of pure and Co_3O_4 loaded SnO_2 nanoparticles with ethanol concentration at RT. The calculated sensitivity for pure and Co_3O_4 loaded SnO_2 are 0.076 and 0.084, respectively. The Co_3O_4 loading enhance the sensitivity of SnO_2 nanoparticles. The surface adsorbed oxygen species is responsible for the ethanol gas detection mechanism of pure SnO_2 . Oxygen molecules in ambient air will adsorb on SnO_2 surface, collecting electrons from the conduction band to produce oxygen species. Thus, an electron depletion layer is been built near the surface of SnO_2 . A reaction

would occur when the ethanol vapor and the SnO₂ gas sensor made contact. The electrons that are captured will eventually return to the SnO₂ conduction band, causing the electron transport barrier to constrict and the electron depletion layer to shrink. Compared to pure SnO₂, the ethanol gas detection method of SnO₂ loaded with Co₃O₄ is distinct. At the interface between SnO₂ and Co₃O₄, nanoscale p-n heterojunctions will form when the two distinct types of metal oxide semiconductors come into contact. The oxygen molecules were adsorbed on the surface of the Co₃O₄-loaded SnO₂ nanoparticles, and electrons were collected to produce oxygen species. Additionally, the p-type Co₃O₄ can trap electrons emitted by SnO₂, leading to an additional depletion layer and potential barrier formed in the heterocontact. The p-n heterojunctions existed on the surface of Co₃O₄ loaded SnO₂ nanoparticles adsorb reductive ethanol vapor and O₂ more easily. According to Zhang *et al.* [20], free electrons move and reach the semiconductor's surface when the charge separation is preserved as a result of the distinct work functions of SnO₂ and Co₃O₄. As a result, there are more free electrons on the surface of Co₃O₄/SnO₂ than SnO₂. Because there are so many free electrons on the semiconductor surface, a large number of oxygen species are adsorbed there as a result of the electrons becoming trapped. When ethanol is passed, CO₂ and H₂O are produced as a result of a reaction between the ethanol molecules and the adsorbed oxygen species that releases the trapped electrons back into the semiconductor. As there are more oxygen species on the surface of SnO₂/Co₃O₄ nanoparticles than on the surface of pure SnO₂ nanoparticles, which have fewer adsorbed oxygen species, more ethanol molecules can reach the surface, improving sensitivity. In addition to this the enhanced sensitivity is attributed to the changes in the texture coefficient of (110) and (200) planes. The reduction in texture coefficient occurred along densely packed (110) plane with concomitant increase in (200) plane. The texture coefficient of (200) planes increase at the cost of (110) planes which results vacancies on (110) plane. Because more vacancies are created on reduced (110) surfaces of Co₃O₄-loaded SnO₂, these surfaces have higher surface energies. This can serve as a better surface for ethanol molecule adsorption because there are numerous unsaturated bonds on the (110) plane, which in turn contributes to a stronger sensor response. Similar outcomes were observed by Kumar *et al.* [36] where the changes in texture coefficient of W-doped SnO₂ modify the morphological, structural and optical properties and it also enhances the sensing property of the material. Wang *et al.* [24] also reported on fluorine doped SnO₂, the doping increases preferred orientation along (200) plane with concurrent decrease along (110), which in turn improves the conductivity of SnO₂. Hence the enhanced sensitivity in Co₃O₄ loaded SnO₂ is attributed to the collective contribution from heterocontact interface and vacancies created along (110) plane.

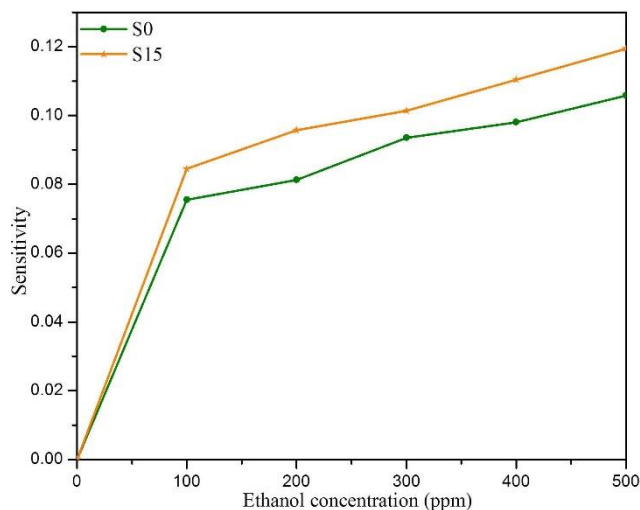


Fig. 10. Spectral response of S0 and S15 toward various (0–500 ppm) ethanol concentrations.

CONCLUSION

Thus, in conclusion, the pure Co₃O₄ loaded SnO₂ nanoparticles were prepared by simple co-precipitation method. The sensor's reaction to the ethanol gas is enhanced by the Co₃O₄ loading. According to the XRD examination, there is a decrease in the textural coefficient of the (110) plane for Co₃O₄ loaded SnO₂, which can lead to the formation of numerous unsaturated bonds across the plane. These bonds subsequently serve as a preferred site for the adsorption of ethanol molecules, resulting in a higher sensing response. The pure SnO₂ with RTFM exhibit a better sensitivity. The enhancement in sensitivity upon Co₃O₄ loading is attributed to the reduction in particle size which increases the surface to volume ratio which leads to more surface vacancies and the nanoscale heterojunction between Co₃O₄ and SnO₂ decreased planar density of (110) plane. The results indicates that the Co₃O₄ loaded SnO₂ nanoparticles are appropriate for the ethanol sensing.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. Stella, C.; Diva Prabhakar, Prabhu, M.; Soundararajan, N.; Ramachandran, K.; *J Mater Sci: Mater Electron*, **2016**, 27, 1636.
2. Stella, C.; Soundararajan, N.; Ramachandran, K.; *Adv. Mater. Lett.*, **2016**, 7, 652.
3. Stella, C.; Soundararajan, N.; Ramachandran, K.; *J Mater Sci: Mater Electron*, **2015**, 26, 4178.
4. Tan, W.; Yu, Q.; Ruan, X.; Huang, X.; *Sens. Actuators B*, **2015**, 212, 47.
5. Jo, K. W.; Moon, S. W.; Cho, W.J.; *Appl. Phys. Lett.*, **2015**, 106, 043501.

6. Birkel, A.; Lee, Y.G.; Koll, D.; Meerbeek, X. V.; Frank, S.; Choi, M. J.; Kang, Y.S.; Char K.; Tremel, W.; *Energy Environ. Sci.*, **2012**, 5, 5392.
7. Huang, X.; Wang, H.; Niu, C.; Rogach, A. L.; *CrystEngComm.*, **2015**, 17, 5593.
8. Li, W.; Shen, C.; Wu, G.; Ma, Y.; Gao, Z.; Xia, X.; Du, G.; *J. Phys. Chem. C*, **2011**, 115, 21258.
9. Tamaekong, N.; Liewhiran, C.; Wisitsoraat A.; Phanichphant, S.; *Sensors*, **2009**, 9, 6652.
10. Buso, D.; Post, M.; Cantalini, C.; Mulvaney, P.; Martucci, A.; *Adv. Funct. Mater.*, **2008**, 18, 3843.
11. Sheini, N.A.; Rohani, M.; *Mater. Sci. Eng.*, **2016**, 108, 012033.
12. Kumar, R.; Khanna, A.; Tripathi, P.; Nandedkar, R. V.; Potdar, S. R.; Chaudhari S. M.; Bhatti, S. S. ; *J. Phys. D: Appl. Phys.*, **2003**, 36, 2377.
13. Jeong, H. M.; Kim, J. H.; Jeong, S. Y.; Kwak, C.H.; Lee, J. H.; *Appl. Mater. Interfaces*, **2016**, 8, 7877.
14. Zhang, L.; Jing, X.; Liu, J.; Wang, J.; Sun, Y.; *Sens. Actuators B*, **2015**, 221, 1492.
15. Bekermann, D.; Gasparotto, A.; Barreca, D.; Maccato, C.; Comini, E.; Sada, C.; Sberveglieri, G.; Devi, A.; Fischer, R. A.; *ACS Appl. Mater. Interfaces*, **2012**, 4, 928.
16. Na, C.W.; Woo H. S.; Lee, J. H.; *RSC Advances*, **2**, 414 (2012).
17. Na, C.W.; Park, S. Y. ; Chung, J. H.; Lee, J. H.; *ACS Appl. Mater. Interfaces*, **2012**, 4, 6565.
18. Woo, H. S.; Na, C. W.; Kim, I. D.; Lee, J. H.; *Nanotechnology*, **2012**, 23, 245501.
19. Wang, L.; Lou, Z.; Zhang, R.; Zhou, T.; Deng, J.; Zhang, T.; *ACS Appl. Mater. Interfaces*, **2016**, 8, 6539.
20. Zhang, M. M.; Jiang, G. S.; *Chin. J. Chem. Phys.*, **2007**, 20, 315.
21. Shi, S.; Gao, D.; Xu, Q.; Yang, Z.; Xue, D.; *RSC Adv.*, **2014**, 4, 45467.
22. Zeng, R.; Wang, J. Q.; Chen, Z. X.; Li, W. X.; Dou, S. X.; *J. Appl. Phys.*, **2011**, 109, 07B520.
23. Liu, J.; Huang, X.; Ye, G.; Liu, W.; Jiao, Z.; Chao, W.; Zhou, Z.; Yu, Z.; *Sensors*, **2003**, 3, 10.
24. Wang, J. T.; Shi, X. L.; Liu, W. W.; Zhong, X. H.; Wang, J. N.; Pyrah, L.; Sanderson, K. D.; Ramsey, P. M.; Hirata, M.; Tsuri, K.; *Sci. Rep.*, **2014**, 4, 3679.
25. Sharma, A.; Singh, A. P.; Thakur, P.; Brookes, N. B.; Kumar, S.; Lee, C. G.; Choudhary, R. J.; Verma, K. D.; Kumar, R.; *J. Appl. Phys.*, **2010**, 107, 093918.
26. Gnanam, S.; Rajendran, V.; *Digest Journal of Nanomaterials and Biostructures*, **2010**, 5, 925.
27. Farhadi, S.; Pourzare, K.; Sadeghinejad, S.; *J. Nanostructure Chem.*, **2013**, 3, 16.
28. Gavrilenko, O. N.; Pashkova, E. V.; Belous, A. G.; *Russian Journal of Inorganic Chemistry*, **2007**, 52, 1835.
29. Mehraj, S.; Ansari, M. S.; Alimuddin, *Physica B*, **2013**, 430, 106.
30. Makhlof, M. T.; Abu-Zied, B. M.; Mansoure, T. H.; *Physical Chemistry*, **2012**, 2, 86.
31. Ahmed, S. A.; *Solid State Commun.*, **2010**, 150, 2190.
32. Dong, Z.; Fu, Y.; Han, Q.; Xu, Y.; Zhang, H.; *J. Phys. Chem. C*, **2007**, 111, 18475.
33. Nethravathi, C.; Sen, S.; Ravishankar, N.; Rajamathi, M.; Pietzonka, C.; Harbrecht, B.; *J. Phys. Chem. B*, **2005**, 109, 11468.
34. Deori K.; Deka, S.; *CrystEngComm*, **2013**, 15, 8465.
35. Cao, F.; Wang, D.; Deng, R.; Tang, J.; Song, S.; Lei, Y.; Wang, S.; Su, S.; Yang, X.; Zhang, H.; *CrystEngComm*, **2011**, 13, 2123.
36. Kumar, M.; Kumar, A.; Abhyankar, A. C.; *ACS Appl. Mater. Interfaces*, **2015**, 7, 3571.

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