Effect of Cobalt Doping on Gas Sensing Properties of SnO₂ Thick Films Prepared by Chemical Co-Precipitation Method

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Co-precipitation method was used for the preparation of undoped SnO₂ and n-type semiconductor nanomaterials of cobalt-doped SnO₂. To identify the crystalline phase and morphology of the nanomaterials were characterized by X-ray powder diffraction and scanning electron microscopy. To focus and study on the gas sensing behaviour of undoped SnO₂ and modified Co-doped SnO₂ thick films. To study there sensitivity among the toxic, flammable and hazardous ethanol, hydrogen sulphide, nitrogen dioxide and ammonia gases. The optimum working temperature for the nanomaterial is same as per the variable gas sensitivity.

Keywords: Co-precipitation, Cobalt-doped, SnO₂, Gas sensor, Sensitivity.

INTRODUCTION

As per the safety environment and to maintain the concentration of toxic and flammable gases those are potentially create the problem in industrial era and their employees health issue not only them but also the peoples those are live near to them [1]. However, the gas sensor given guarantee to healthy environment, safe production and have ability to identify the specific gas from the type of chemical gases even the concentration of the gas is very small [2]. Metal oxides especially doped metal oxides has been utilized as gas sensing material because this dopant controlling the electrical, optical and constructive properties of material and which act as charge carrier to help an enhance the electricity supply due to the demand of industrial era those are having the huge potential applications in daily life [3].

The sensitivity property of metal oxides has been improved with the help of additive in the metal oxides by reducing the particle size or by changing the functioning temperature, here humidity also effect on the metal oxide sensitivity [4,5]. The gas molecule oxidation and reduction nature also show valuable effect on gas sensing material [6]. For the development of highly sensible gas sensing material the dimension of the material is very important or considerable because of specific geometry with small grain size to generate the large surface area which help to develop the good interconnection between the gas and metal oxides hence the nanotechnology is a significant role in the field of gas sensors [7]. The sensors are having numerous advantages such as small size, high reliability, low budget and low power consumption [8]. SnO₂ has exceptional chemical stability, optical stability, electrical conductivity, and a wide band gap of 3.6 eV at ambient temperature [9,10]. There have been numerous methods investigated to improve the sensing capability of pure SnO₂, including coating with a noble metal such as (Au, Pt and Pd) to act as a sensitizer [11-13]. Due to the high cost of noble metals, it raises the price of making sensors. To overcome this problem, another flexible method to enhance the gas sensing capabilities of pure SnO₂ is to either load or dope it with another metal oxide to create a SnO₂ nanocomposite [14,15].

The sensor's mechanism is an oxidation-reduction reaction between the target gas and the SnO₂ surface, resulting in a change in SnO₂ resistance with gas concentration [16]. In comparison to other metal ions, cobalt has inhibitory effects on crystalline development and assumes a crucial part in the detecting capabilities of sensors. Furthermore, cobalt demonstrates inherent

attributes of excellent corrosion resistance, ferromagnetism and adequate thermal and electrical conductivity. The SnO_2 has ionic radii of Co_2 (0.58 Å), and Sn_4 (0.64 Å) the ionic radius of Co_2 is less than that of Sn_4 [17]. Consequently, it is possible to anticipate the substitution of Co ions at the Sn^{4+} site within the SnO_2 system. Consequently, there is an elevation in oxygen deficit and a reduction in the grain size of SnO_2, both of which are anticipated to impact the characteristics of pure SnO_2. In this study, a Co dopant has been used to alter the electrical characteristics of SnO_2 and enhance its gas sensing capabilities.

EXPERIMENTAL

Synthesis of Co doped SnO_2 nanomaterials: Sample with normal composition of Co doped SnO_2 were synthesized by using the co-precipitation method. First colloidal solution was prepared with $SnCl_4 \cdot 5H_2O$ with deionized water stirring for 1 h at room temperature. After the preparation of colloidal solution, added $CoCl_2 \cdot 2H_2O$ with constant stirring for 1 h and then required amount of NH_4OH were added dropwise with constant stirring to maintain the pH 9 of mixture. For chemical homogeneity, the dropping rate was regulated as 5 drops per second. The solution was then mixed under constant stirring for 2 h until the precipitate were formed. The mixture was filtered on simple filter paper and then washed with three or five times with deionized water. Then resulting mixture was again washed with deionized water followed by the drying the mixture in oven for 2 h at 80 ºC in order to remove the excess chlorine. The obtained material was grounded into fine powder in mortal and piston and annealed at 500 ºC for 2 h in muffle furnace under air.

Fabrication of Co-doped SnO_2: Screen printing is a cost effective technique where the mesh was used to prepare the thick film of the material on the substrate [18]. Here, a ratio 30:70 of organic to inorganic materials was used. The organic material acts as a binder which was made up from butyl carbitol acetate (BCA) and ethyl cellulose and used to fix the particle doped nanomaterial onto the glass surface. To prepare the fine nanoparticles of Co-doped SnO_2, 0.7g of Co doped SnO_2 was grinded with the pinch of ethyl cellulose for 30 min followed by the addition of BCA dropwise in order to obtain a smooth paste. Then this pseudo-plastic paste was spread over 20 thick layers were made over a cut piece glass having 3 cm × 1.5 cm. After that dry this film for 45 min in infrared lamp and then heated for 2 h at 500 ºC in a muffle furnace. After room temperature cooling at next day, thick film sensors materials were used for exciting gas sensing properties.

Characterization: The elemental analysis and surface morphology of the synthesized material were investigated by JEOL-JEM 2300 (LA) scanning electron microscope instrument having an electron dispersion spectroscope (SEM-EDS) facility. The X-ray powder diffraction analysis were carried out by Phillips X-ray diffractometer in a diffraction angle range $2\theta = 10$ to 80º using Cu$K\alpha$ radiation with a wavelength of 1.540598 Å.

RESULTS AND DISCUSSION

SEM and EDS analysis: The scanning electron microscopy (SEM) images exhibit a high degree of nanoparticle aggregation, characterized by a closely packed arrangement, together with a micro-surface that displays roughness and porosity (Fig. 1). Furthermore, it was observed that both undoped SnO_2 and Co-doped SnO_2 exhibit the presence of minute gaps or cavities on their respective surfaces, which are distributed throughout the material. These voids can serve as highly effective adsorbents in the context of gas sensing research. The gas sensing capacity of specific sensors can
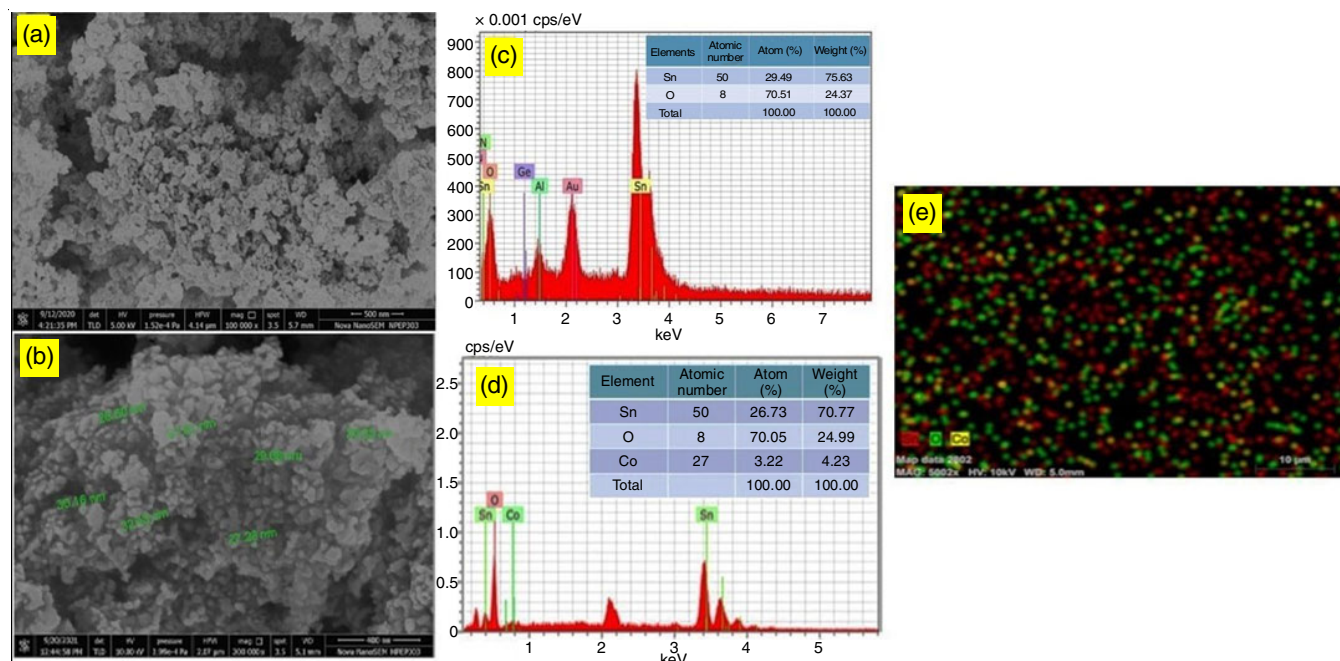

Fig. 1. SEM images of (a) undoped SnO_2, (b) Co-doped SnO_2, (c) EDS spectra of undoped SnO_2, (d) EDS spectra of Co-doped SnO_2, EDS report of mapped data and (e) Co-doped SnO_2 nanoparticles

be enhanced by the occlusion of smaller adsorbate gas molecules across the surface through chemisorption or physisorption [19].

The effective confirmation of doping of cobalt in SnO_2 was achieved by the utilization of elemental mapping analysis. Fig. 1e illustrates the observation of the presence of dopant on the SnO_2 matrix.

XRD studies: The structural arrangements of Co-doped SnO_2 were studied using PXRD at the angle of 2θ between 10º to 80º. The Co doped SnO_2 shows several Bragg's reflection peak at different 2θ angle of 26.70º, 34.00º, 38.11º, 51.97º (Fig. 2), which can be indexed to (110), (101), (020) and (121) planes, respectively. The observed diffraction peak were observed as orthorhombic structure [20]. Here, the grain size of the synthesized material Co-doped SnO_2 was calculated by using Debye-Scherrer's equation $T = 0.94\lambda/\beta Cos\ \theta$, where T = average particle size, λ = wavelength, θ = Diffraction angels, β = full-width half maximum. The obtained average particle size (T) was found to be 17.9 nm.
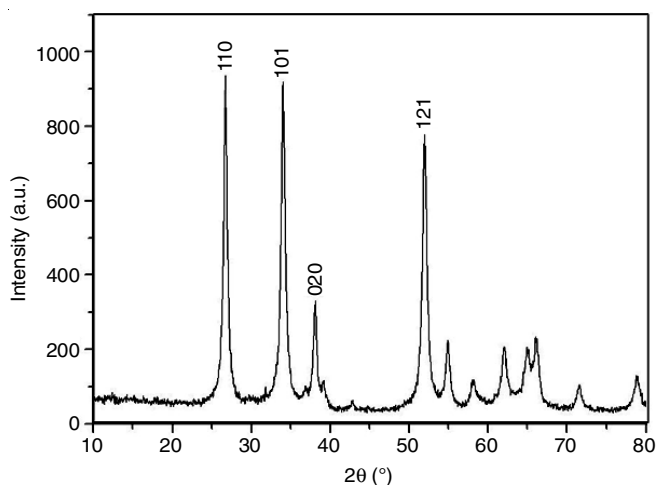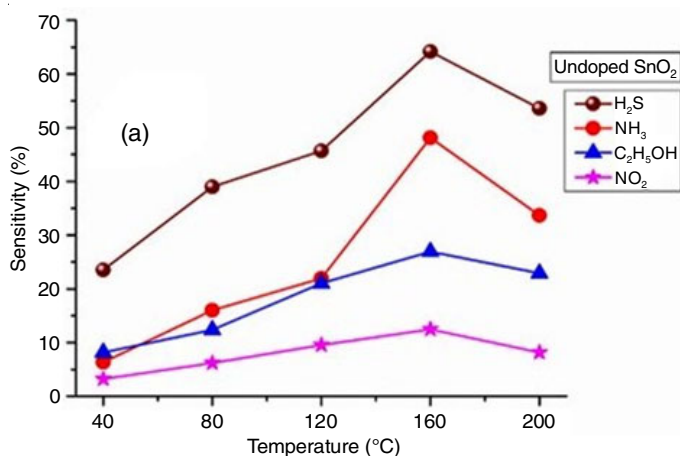

Fig. 2. XRD pattern of Co-doped SnO₂

Gas sensing properties of undoped and Co-doped SnO₂ thick films: The gas sensors employed in this study were screen printed thick films consist of undoped SnO_2 and Co-doped SnO_2. These films were specifically designed to detect hazardous gases like H_2S, NH_3, C_2H_5OH and NO_2 under optimum conditions.

Optimum operating temperature condition: The most important property of prepared gas sensor material is the operating temperature because it gives information about the gas sensing process of the gas towards the surface of the material [21]. Fig. 3 shows the optimum gas response at the temperature ranged from 200 to 40 ºC cooling cycle. The response curves show the gas response for undoped SnO_2 for tested gases like H_2S, NH_3, C_2H_5OH and NO_2. The undoped SnO_2 sensor exhibited a significant response to hydrogen sulphide (H_2S) vapours at 120 ºC with a recorded response rate of 64.20%. Similarly at 160 ºC, the sensor also give a response rate of 48.40% to NH_3 gas, 20% to C_2H_5OH gas vapours and 10% to NO_2 vapours (Fig. 3a). These findings highlighted the sensitivity of undoped SnO_2 sensor towards various gases at different operating temperatures. Simultaneously Fig. 3b shows the Co-doped SnO_2 sensor response for the same gases, out of which the highest the response was recorded for C_2H_5OH vapours at 120 ºC with 68.30% response, then 35.20% response was recorded for H_2S gas at 120 ºC, NO_2 gas vapours showed a 12.20% response at 120 ºC and NH_3 vapours showed 7.20% at 120 ºC for Co-doped SnO_2 sensor.

Fig. 4 shows the maximum response in undoped and Co doped gas sensors have been given by H_2S and ethanol vapours, respectively. The selectivity of other gases was calculated in ratio with respect to H_2S for undoped SnO_2 sensor and C_2H_5OH for Co-doped SnO_2 sensor. Thus, H_2S is highly selective for undoped SnO_2, while C_2H_5OH is selective for Co-doped SnO_2 gas sensors.

The concentration of gas variation and response recorded for undoped SnO_2 and Co-doped SnO_2 are shown in Fig. 5. A linear relationship for tested gas H_2S for undoped SnO_2 sensor and C_2H_5OH for Co-doped SnO_2 was found upto 300 ppm gas concentrations for both the sensors. It can be seen that there is gradual increase in the gas response for 100 ppm to 300 ppm for undoped SnO_2 and Co-doped SnO_2 sensors. However, a sharp decline in the sensitivity from 300 ppm to 500 ppm gas concentration in both sensor was also observed.

Another two properties of gas sensor are the response time and recovery time. Fig. 6 shows the response and recovery time
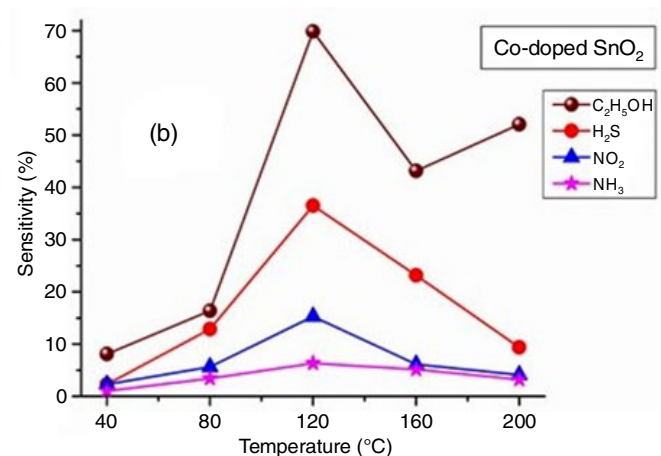

Fig. 3. Gas response of tested gases at a specific temperature for (a) undoped SnO₂ and (b) Co-doped SnO₂ thick film sensor
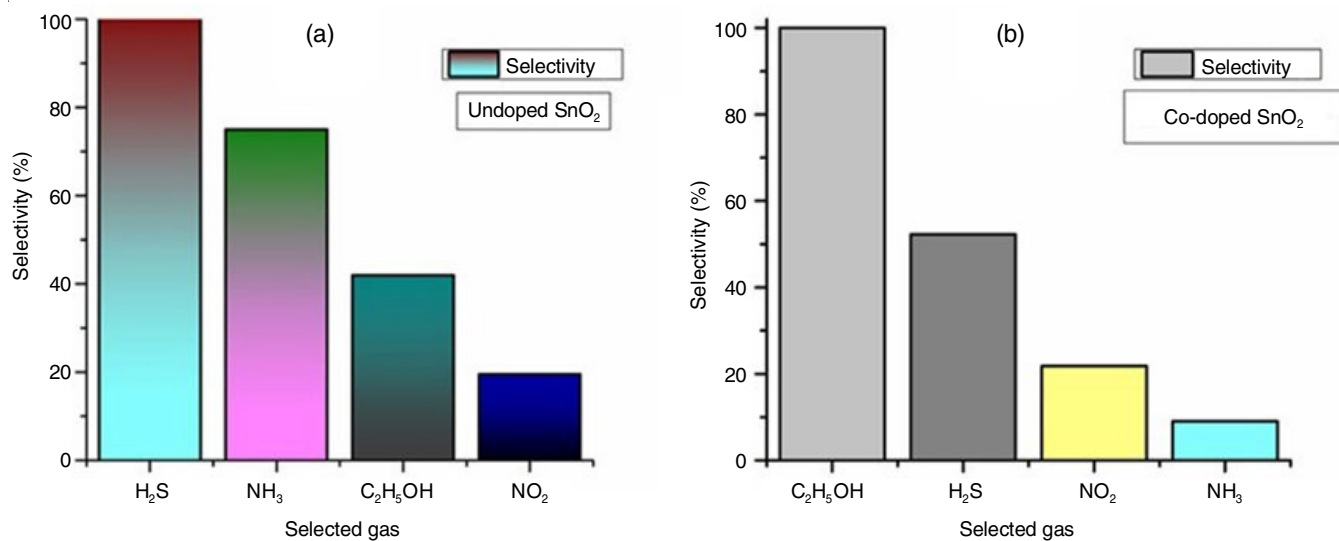
Fig. 4. Graphical representation of response of (a) undoped SnO_2 and (b) Co doped SnO_2 sensors for various gases
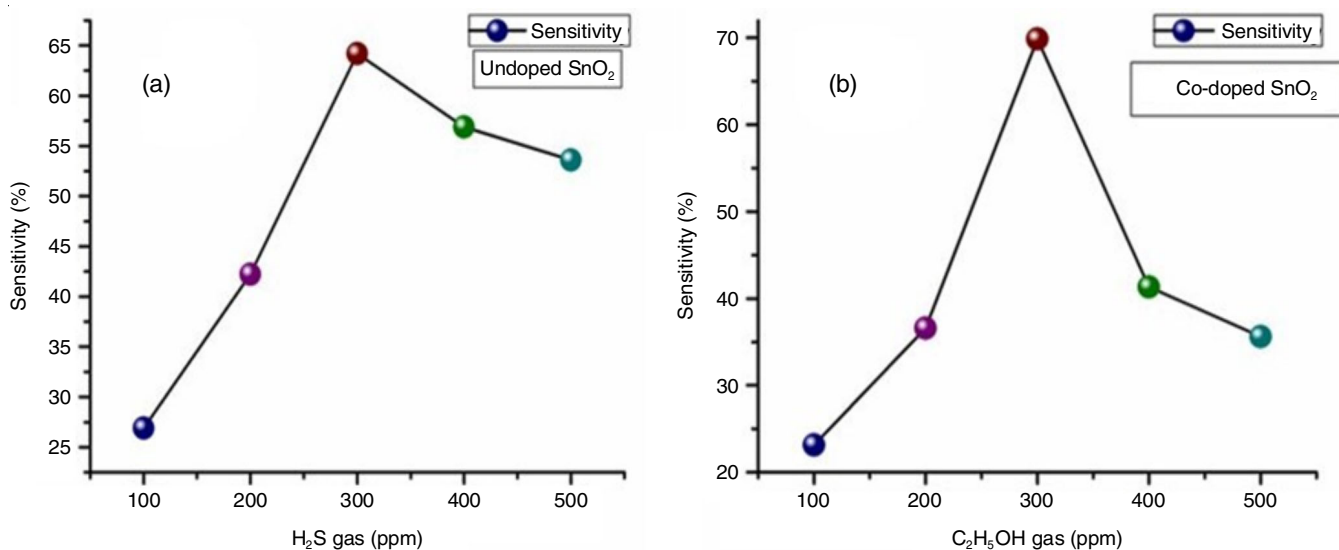

Fig. 5. Gas concentration in ppm variation for (a) undoped SnO_2 and (b) Co-doped SnO_2 sensor
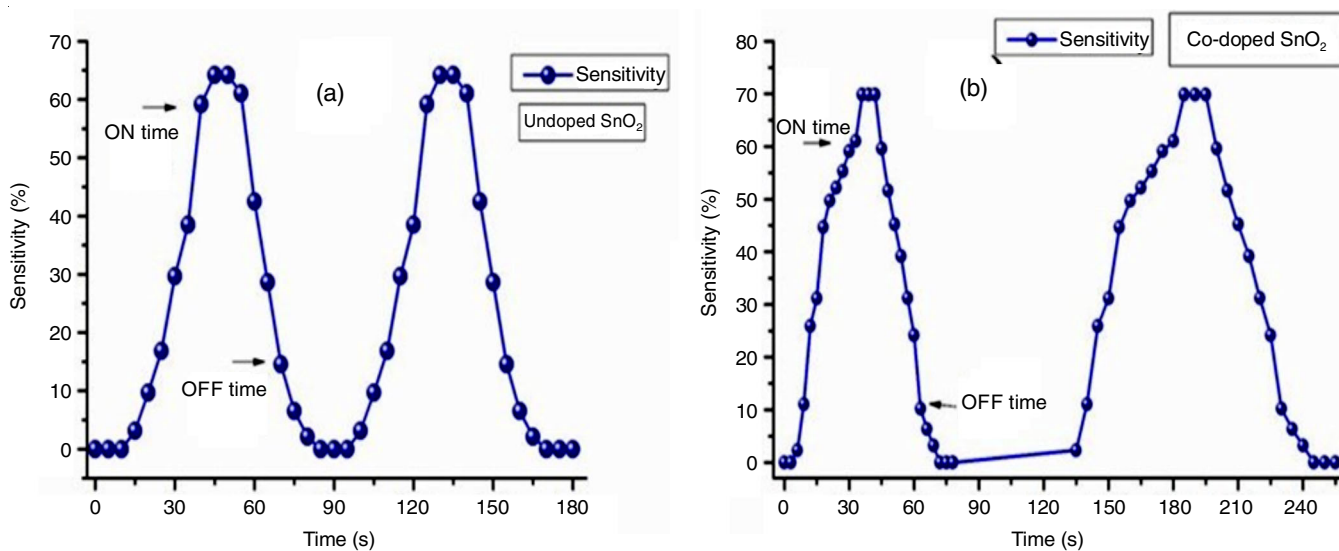

Fig. 6. Response and recovery time of (a) undoped SnO_2 and (b) Co-doped SnO_2 gas sensor

of the both gas sensors working at the optimum temperature, with gas concentration of 50 µg/L at 40 ℃ and humidity 20%. The transient response characteristics of undoped SnO_2 thick film towards 300 ppm of H_2S at the optimum temperature of 160 ℃ shows the fast response of 35 s and recovery time 70 s. Whereas the transient response characteristics of Co-doped SnO_2 sensor towards 300 ppm of C_2H_5OH at 120 ℃ exhibited the response time of 30 s and a recovery time of 40 s. The enhanced response and recovery time in Co-doped SnO_2 can potentially be attributed to due the heightened reactivity of C_2H_5OH vapour with adsorbed oxygen in the presence of Co sites on the surface as well as the high porous structure of the sensor. Enhanced gas diffusion through the grain boundaries would facilitate prompt oxidation of gas, resulting in a rapid response. The response and recovery durations of sensors are the crucial characteristics in determining their suitability for various applications.

In order to evaluate the stability and reproducibility of the undoped and Co-doped SnO_2 sensors, we conducted measurements of its response to an H_2S concentration of 300 ppm at 160 ℃ for undoped SnO_2 sensor. For Co-doped SnO_2 sensor, we measured their response to a C_2H_5OH concentration of 300 ppm at 120 ℃ on the 5th, 10th, 15th, 20th, 25th and 30th day following the initial measurement. Fig. 7 demonstrates that both undoped SnO_2 and Co-doped SnO_2 sensors had a response rate of around 95% of their initial performance on the 30th day. This result demonstrates the stability and reproducibility of the sensor material, which favours its use in the industrial settings [22].

In the comparative study of undoped SnO_2 and Co-doped SnO_2, it was observed that as undoped SnO_2 have less response than Co-doped SnO_2 for NH_3, H_2S, NO_2 and C_2H_5OH vapours. In literature, different methods has been reported for the preparation of Co-doped SnO_2 having different sensing properties for different gases as well as volatile vapours (Table-1).

TABLE-1
COMPARATIVE STUDY OF UNDOPED SnO₂ AND Co-DOPED SnO₂ WITH DETECTED GASES

Sample	Analyzed gas	Operating temp. (℃)	Response (%)
Undoped SnO₂	H₂S	120	64.20
	NH₃	160	48.40
	C₂H₅OH	160	20
	NO₂	160	10
Co-doped SnO₂	H₂S	120	35.20
	NH₃	120	7.20
	C₂H₅OH	120	68.30
	NO₂	120	12.20

Furthermore, a number of researchers have documented the sensing capabilities of Co-doped SnO_2 in relation to NH_3 and C_2H_5OH gases. These studies have explored the impact of varying Co-doped SnO_2 through the utilization of diverse synthesis techniques. However, it is important to emphasize that these investigations necessitated higher concentrations in parts per million (ppm) compared to the reported findings with the present research work. Hence in this work, Co-doped SnO_2 get the good results as compare to earlier reported similar material (Table-2). In literature, the co-doped SnO_2 with other gases such as H_2S and NO_2 has been previously described, specifically in case of Co-doped SnO_2 [26] and In-doped SnO_2 [27]. However, in this study, we present the first report on the
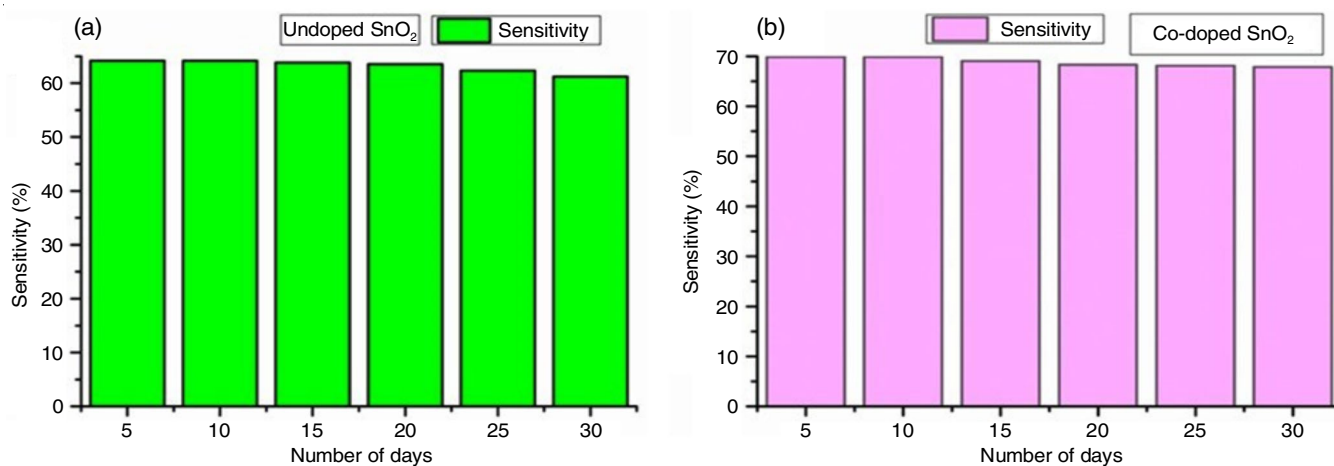

Fig. 7. Gas sensing material response

TABLE-2
SENSING PROPERTIES OF Co-DOPED SnO₂ WITH AVAILABLE LITERATURE REPORT

Samples	Synthesis method	Gas analyte	Opera. temp	Conc. (ppm)	Response	Retention time	Ref.
0.5-3 wt% Co-doped SnO₂	Co-precipitation	C₂H₅OH	250	2000	120	3s/15s	[23]
Graphine supported Co-doped SnO₂	Flame spray pyrolysis	C₂H₅OH	350	1000	2147	1s	[24]
5 mol %	Solvothermal	NH₃	28	150	10.7	10s/150s	[25]
Co-doped SnO₂	Co-precipitation	H₂S	120	300	35.20	–	Present work
Co-doped SnO₂	Co-precipitation	NO₂	120	–	12.20	–	Present work

modification of SnO_2 with cobalt and observed the encouraging results.

Conclusion

In this work, undoped and Co-doped SnO_2 nanomaterials were synthesized by the chemical co-precipitation method. After annealing at 500 ºC, both sensors were investigated for the sensing of four different gases *viz.* NH_3, H_2S, NO_2 and C_2H_5OH. The thick films of undoped and Co-doped SnO_2 were prepared by screen-printing technology. The good responses for H_2S and C_2H_5OH gases were recorded for undoped SnO_2 and Co-doped SnO_2. For undoped SnO_2 sensor, the gas response was recorded to be 64.20% at 160 ºC for H_2S gas. The gas response of Co-doped SnO_2 shows gas response towards C_2H_5OH to be 68.30% at 120 ºC. The enhanced gas response in the Co-doped SnO_2 sensors compared with the undoped SnO_2 is due to decreased band gap energy, more surface area and improved active site. Finally, it can be concluded that Co-doped SnO_2 sensors is an effective sensor at moderately high temperatures for C_2H_5OH vapours.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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