



Fe-incorporated ZnO-TiO₂ Nanocomposites for Improved CO₂ Sensing

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ABSTRACT

The nanoscaled ZnO-TiO₂ and Fe-incorporated ZnO-TiO₂ nanocomposite powders were synthesized via hydrothermal route at 120°C and characterized for their potential use in gas sensing application. Both ZnO-TiO₂ and Fe-incorporated ZnO-TiO₂ nanocomposites exhibit crystalline phases corresponding to hexagonal wurtzite ZnO and anatase TiO₂. The average crystallite size of ZnO-TiO₂ and 0.1, 0.2, 0.3, 0.4, 0.5 Fe-incorporated ZnO-TiO₂ nanocomposites was determined to be 40.40, 31.36, 39.42, 30.62, 31.57, 29.73 nm, respectively. Formations of Zn-O-Ti bonds and Ti-O or Zn-O were confirmed by FTIR. Scanning electron microscopy images showed uniform porous grains of nanocomposites. The homogeneous incorporation of Fe without the formation of secondary iron phases and additional oxygen vacancies in Fe-doped samples were confirmed by EDAX. The thick film of ZnO-TiO₂ and Fe-incorporated ZnO-TiO₂ nanocomposites were fabricated using a traditional screen printing setup. Thick films exhibited a nonlinear I-V behavior, indicative of hybrid nature of the nanocomposites. The average thickness of undoped ZnO-TiO₂ nanocomposite was found to be 30 µm. The CO₂ sensing response with different compositions of Fe-incorporated ZnO-TiO₂ results determined that 0.5 mol% Fe-incorporated ZnO-TiO₂ nanocomposites (FZT₅) showed the highest response to 286 ppm at ~280°C. Therefore, Fe-doped ZnO-TiO₂ nanocomposites can be effective materials for real-time CO₂ detection with excellent response and recovery times.

Keywords: ZnO; TiO₂; nanostructures; CO₂; Gas sensor; Hydrothermal synthesis; Air pollution.

1. INTRODUCTION

Recent advancements in gas sensor technology are increasingly aimed at creating smart, selective, sensitive, and energy-efficient devices for real-time monitoring in both environmental and industrial setup. Carbon dioxide has adverse impacts on climate, workplace safety, and indoor air quality. To maintain food safety, optimal growth in agriculture, and healthy indoor quality, it is essential to monitor CO₂ levels. Also, it is essential to track and regulate CO₂ emissions from the industrial plant in order to reduce their environmental impact (Abdelkarem *et al.* 2023; Kanaparthi and Singh, 2019; Kumar *et al.* 2023). Gas chromatography, infrared (IR) spectroscopy, and fluorescence spectroscopy are the optical techniques traditionally used for measuring CO₂ (Arias *et al.* 2025; Yu and Obrovac, 2019; Wang *et al.* 2017). Despite their accuracy, these techniques are not appropriate for real-time, on-site CO₂ monitoring due to their high costs, massive size, and immobile nature. As the result, gas sensors based on metal oxide semiconductors (MOS) have undergone extensive research due to their easy fabrication, affordability, and compatibility with compact electronic devices (Haygood *et al.* 2024; Taha *et al.* 2024; Ahmad *et al.* 2024). Notwithstanding the advantages of ceramic materials such as zinc oxide (ZnO) and titanium dioxide (TiO₂), these materials exhibit suboptimal performance in

detecting CO₂. This limitation arises mainly from the relatively low adsorption energy of CO₂ on the surfaces of metal oxides, combined with insufficient charge transfer efficiency, which results in reduced sensitivity and selectivity.

ZnO and TiO₂ are recognized as wide-bandgap semiconductors with remarkable chemical stability and high surface reactivity. Their nanostructured forms are particularly promising for gas sensing applications due to their enhanced surface-to-volume ratios (Tsai *et al.* 2018; Cao *et al.* 2022). Moreover, the incorporation of ZnO and TiO₂ into nanocomposites leads to the formation of heterojunctions at their interfaces, which improve charge carrier separation, modify depletion layer behavior, and enhance surface reactivity. This synergistic effect significantly contributes to the enhancement of gas sensing performance (Ortiz-Quinonez and pal, 2024; Kalyamwar and Raghuwanshi, 2013).

Recent studies show that the incorporation of transition metals, such as iron into these nanocomposite materials considerably influences their structural, electronic, and catalytic characteristics (Davoodi and Shafeeyan, 2024; Tseng *et al.* 2016). Fe³⁺ ions play a key role in increasing oxygen vacancies, which in turn affect grain growth and enhance the adsorption-desorption dynamics by raising the density of surface defects. These

combined factors improve gas sensitivity and lead to faster response and recovery times. Furthermore, Fe doping facilitates the tuning of the band structure and Fermi level alignment, thereby optimizing the interaction between the sensor material and the target gas molecules (Zhang *et al.* 2010; Tong *et al.* 2020; Mardare *et al.* 2017). Improving the performance of MOS-based CO₂ sensors requires careful control of microstructural parameters such as grain size, porosity, crystallinity, and phase composition through a tunable synthesis approach. This control ensures efficient dopant incorporation and promotes the development of nanoscale interfaces that act as active sites for gas interactions.

In this study, ZnO-TiO₂ (ZT) and Fe-doped ZnO-TiO₂ nanocomposites (FZT₁-FZT₅) have been prepared using a hydrothermal method to improve microstructural properties and gas-sensing properties. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDAX) were used to identify the structural properties, chemical composition, morphology, and elemental distribution of the prepared nanocomposites, respectively. Measurements of gas response were conducted to understand the impact of Fe doping on CO₂ sensing.

2. EXPERIMENTAL

2.1 Materials

Zinc oxide and titanium (IV) oxide were sourced from S. D. Fine Chem. Ltd. Iron (III) chloride and sodium hydroxide (NaOH) were obtained from Merck Specialities Private Limited. All reagents were of analytical grade with high purity. Deionized water and ethanol served as solvents throughout the synthesis process.

2.2 Synthesis of ZnO-TiO₂ and Fe-Doped ZnO-TiO₂ Nanocomposites

ZnO-TiO₂ nanocomposite and Fe-doped ZnO-TiO₂ nanocomposite powders were synthesized using a hydrothermal method as depicted schematically in Fig. 1. A nanocrystalline powder mixture of zinc oxide (ZnO) and titanium dioxide (TiO₂) in a 7:3 molar ratio was dispersed in 100 mL of distilled water under continuous magnetic stirring using a Remi-2ML stirrer for 30 minutes. To adjust the pH to approximately 12, a 2 M NaOH solution was added dropwise under stirring, followed by an additional 30 minutes of agitation to ensure complete homogenization. The resulting suspension was then poured into a 500-mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 120°C for 10 hours. Once it naturally cooled to room temperature, the precipitate was separated by centrifugation at 4000 rpm using a Remi R-23 centrifuge.

The collected product was thoroughly washed five times with alternating rinses of deionized water and ethanol to remove residual ions and unreacted species. The washed powders were then dried at room temperature, followed by thermal treatment at 220°C for 14 hours in an i-Therm furnace to remove moisture and enhance structural integrity. For Fe doping, FeCl₃ was added in varying molar concentrations (0.1-0.5 mol%) to the precursor solution prior to pH adjustment, and the synthesis procedure was repeated under identical conditions. The final products were labeled as ZT for the undoped ZnO-TiO₂ nanocomposite and FZT₁ to FZT₅ for Fe-doped nanocomposite containing 0.1, 0.2, 0.3, 0.4, and 0.5 mol% of Fe, respectively.

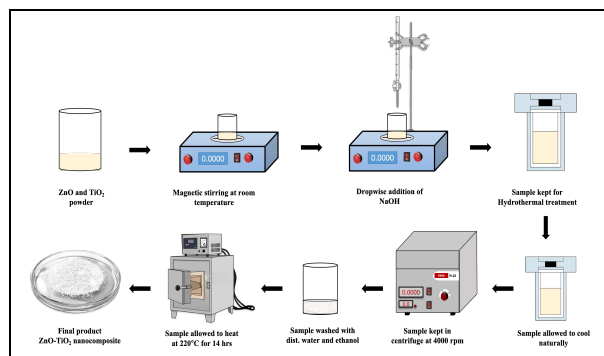


Fig. 1: Hydrothermal synthesis of ZnO-TiO₂ nanocomposite

2.3 Characterization Details

The crystal structure of the synthesized products was characterized by XRD with a Rigaku D/Max-2550 V diffractometer (Cu-K α radiation, $\lambda=1.54178$ Å, Rigaku, Japan). FT-IR spectroscopy was performed using an IR Affinity-1 spectrometer (Shimadzu, Japan). The morphology and microstructure of the product was observed by field emission scanning electron microscopy (FESEM) on a JSM-6380A (JEOL-Japan) microscope operating at an accelerating voltage of 15 kV. The energy dispersive X-ray spectrometry (EDS) study was carried out using an FE-SEM attachment (JEOL-Japan).

3. RESULTS

3.1 X-Ray Diffraction Analysis

The crystallographic structure and microstructural characteristics of the undoped ZT and Fe-doped FZT₁-FZT₅ with Fe content ranging from 0.1 to 0.5 mol%, were investigated using X-ray diffraction (Fig. 2 (a) and (b)). The XRD patterns were recorded over a 2 θ range of 20° to 80°. The undoped nanocomposite ZT exhibited diffraction peaks indexed to the hexagonal wurtzite phase of ZnO (JCPDS No. 23-00450) and the anatase phase of TiO₂ (JCPDS No. 90-15929). Specifically, prominent reflections observed at 2 θ $\approx$ 31.7°, 34.4°, and 36.2° correspond to the (100), (002), and (101) planes of ZnO, while the peaks at 2 θ $\approx$ 25.3°,

36.9°, and 48.0° are attributed to the (101), (103), and (200) planes of TiO₂, respectively. The presence of both ZnO and TiO₂ phases across all samples confirms the successful formation of a binary nanocomposite and the retention of individual crystal structures. The absence of merged or intermediate peaks indicates that ZnO and TiO₂ exist as distinct crystalline domains within the composite.

Moreover, the consistent appearance of Fe-related diffraction peaks observed at $2\theta \approx 55.6^\circ$, 68.3° , and 69.5° correspond to the (124), (117), and (215) planes, respectively, (JCPDS No. 81-03887) across all Fe-doped samples (FZT₁-FZT₅). This confirms the successful incorporation of Fe ions into the ZnO-TiO₂ lattice. Although less intense Fe-associated peaks were detected, no distinct secondary phases such as Fe₂O₃ or Fe₃O₄ were observed, suggesting that Fe was predominantly integrated into the host lattice rather than forming separate impurity phases. Additionally, variations in peak broadening, intensity, and slight shifts in lattice parameters with increasing Fe content point toward lattice strain and structural distortion induced by Fe substitution. These changes support the formation of a doped solid solution without compromising the phase integrity of the ZnO-TiO₂ nanocomposite system (Alizadeh and Baseri, 2022; Davoodi and Shafeeyan, 2024). The average crystallite size (D) of the synthesized samples was estimated using the Debye-Scherrer equation (Onkar *et al.* 2020)

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \dots (1)$$

where k is the shape factor (0.9), λ is the X-ray wavelength (1.5406 Å for Cu K α), β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle. Dislocation density (δ), which indicates the extent of crystallographic defects, was determined using the below formula (Yogasaraswathi and Dheepa, 2023).

$$\delta = \frac{1}{D^2} \quad \dots (2)$$

Table 1 presents the crystallite sizes, dislocation densities, and lattice parameters for all samples studied. The undoped sample (ZT) exhibited a crystallite size of 40.40 nm along with a lower dislocation density of 6.13×10^{14} lines/m². With Fe doping, there was a noticeable decrease in crystallite size; this reduction reached as low as 29.73 nm at the highest Fe concentration found in sample FZT₅. Simultaneously, an increase in dislocation density was noted. These values surpassed 10×10^{14} lines/m² for FZT₁ through FZT₅, indicating more structural defects and grain boundaries were formed. These microstructural changes are beneficial for gas sensing applications because they enhance surface defect density and active sites that promote better gas adsorption and interaction capabilities. Notably, materials with

smaller crystallites and elevated dislocation densities showed improved responses to CO₂ detection.

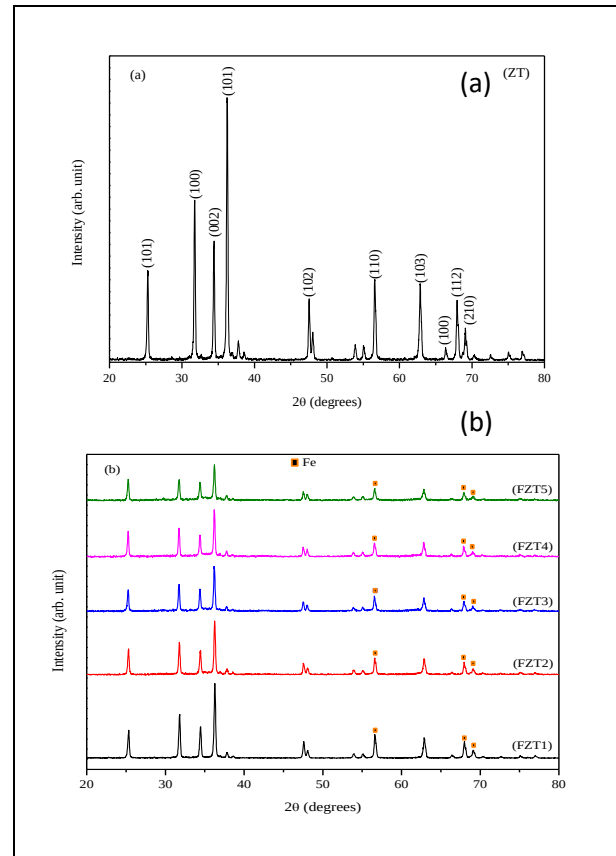


Fig. 2: XRD patterns (a) ZnO-TiO₂ nanocomposites (ZT) (b) Fe-doped ZnO-TiO₂ nanocomposites (FZT₁-FZT₅)

3.2 Fourier Transform Infrared Analysis

Fourier Transform Infrared spectroscopy was performed in the range 3900-400 cm⁻¹ to examine the surface chemical composition of the synthesized nanocomposites. Fig. 3 displays the corresponding FTIR spectra for both undoped ZnO-TiO₂ and Fe-doped ZnO-TiO₂ nanocomposites (FZT₁-FZT₅). All spectra exhibit a broad absorption band at 3200 cm⁻¹ and 3500 cm⁻¹, indicating O-H stretching vibrations. This finding suggests hydroxyl groups are present, which is typically linked to surface hydroxylation vacancies (Mazinani *et al.* 2023). The intensity of this band varied with Fe doping, indicating a greater formation of oxygen vacancies that improve the material interaction with CO₂. The absorption bands observed in the range between 400 cm⁻¹ and 700 cm⁻¹ are linked to Ti-O or Zn-O bond stretching and bending vibrations within the -O-Ti-O-network (Deshmane *et al.* 2015). In the FTIR spectra of Fe-doped ZnO-TiO₂ nanocomposites, small shifts in the vibrational modes indicate changes in the metal-oxygen bonds, which may alter the bonding environments. The peaks observed around 800 cm⁻¹ and 900 cm⁻¹ are linked to the vibration modes of Zn-O-Ti bonds (Karthik *et al.*

2010; Amouzesh *et al.* 2024). The incorporation of Fe into the ZnO-TiO₂ nanocomposites, as indicated by this band, results in a more complex bonding environment,

which enhances the structural and electronic properties of the composite material, rather than disrupting the fundamental interaction between ZnO and TiO₂.

Table 1. Calculated crystallite size, dislocation density, and lattice parameters of undoped and Fe-doped ZnO-TiO₂ nanocomposites

Composition (ZnO:TiO ₂ :Fe)	Lattice Parameters (nm)		Dislocation Density (δ) ($\times 10^{14}$ lines/m ²)	Average crystallite Size (nm)	Gas Sensing Potential
	a=b	c			
7:3:0.0 (ZT)	3.2493	5.2057	6.13	40.40	Moderate
7:3:0.1 (FZT ₁)	3.2493	5.2057	10.16	31.36	High
7:3:0.2 (FZT ₂)	13.9094	21.6040	6.44	39.42	Moderate
7:3:0.3 (FZT ₃)	5.1346	11.3465	10.67	30.62	High
7:3:0.4 (FZT ₄)	13.8250	7.1000	10.03	31.57	High
7:3:0.5 (FZT ₅)	13.8250	7.1000	11.30	29.73	Very High

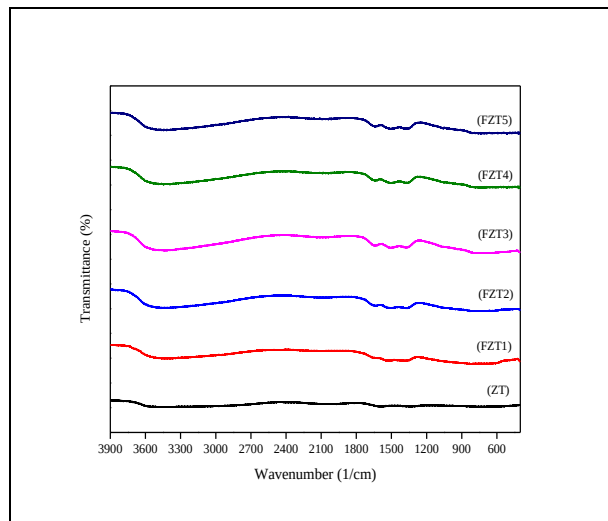


Fig. 3: FTIR spectra of undoped ZnO-TiO₂ (ZT) and Fe-doped ZnO-TiO₂ nanocomposites (FZT₁-FZT₅)

3.3 Scanning Electron Microscopy Analysis

Scanning electron microscopy was employed to analyse the surface morphology and microstructural evolution of ZT and Fe-doped variants (FZT₁-FZT₅). Fig. 4 represents micrographs for all six samples, providing a visual comparison of how different levels of Fe doping affect particle size, grain structure, and surface texture. The scanning electron micrographs for the undoped sample ZT in Fig. 4 (a) shows relatively large grains with an irregular shape that are loosely packed together and moderate agglomeration. This configuration results in a moderately porous surface that facilitates gas diffusion but may restrict active site availability due to lowered specific surface area. In contrast, in the Fe-doped samples, which exhibit spherical or rod-like shapes

depending on increasing iron content, there is a visible decrease in particle size.

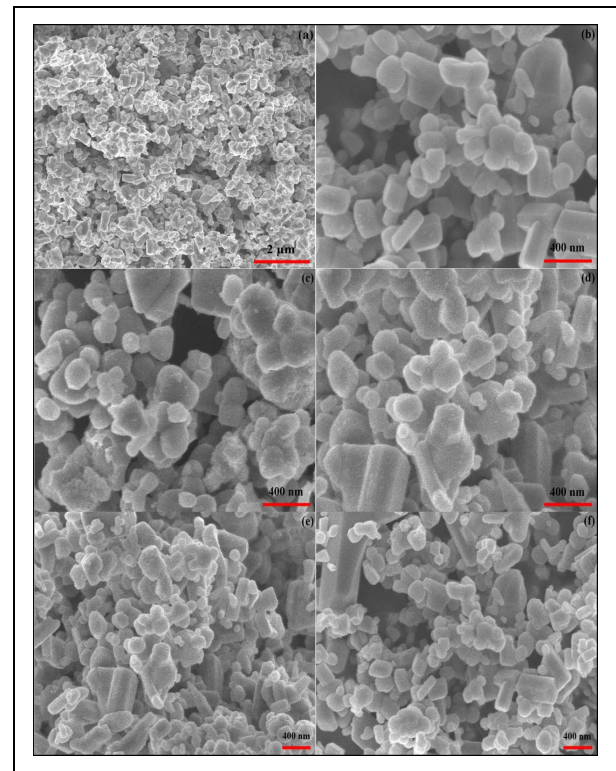


Fig. 4: SEM micrographs of ZnO-TiO₂ nanocomposites: (a) undoped sample (ZT), (b) 0.1 mol% Fe-doped (FZT₁), (c) 0.2 mol% Fe-doped (FZT₂), (d) 0.3 mol% Fe-doped (FZT₃), (e) 0.4 mol% Fe-doped (FZT₄), and (f) 0.5 mol% Fe-doped (FZT₅)

Samples FZT₁ to FZT₅ in Fig. 4 (b-f), reveal more compact microstructure composed of finer grains and denser agglomerates. Particularly in FZT₃ to FZT₅,

the grains are significantly smaller, with more pronounced surface roughness and well-developed intergranular voids. The reduction in particle size and increase in surface roughness with Fe doping can be attributed to the inhibition of grain growth during synthesis. The incorporation of Fe ions introduces lattice strain and defects, which disrupt normal crystal development and promote the formation of smaller, highly defective grains. A rough and more porous surface enhances the adsorption of gas molecules and provides more active sites for gas-solid interactions. As a result, the Fe-doped samples, especially FZT₃ and FZT₅, demonstrate improved sensing characteristics, correlating well with their enhanced CO₂ detection performance.

3.4 Energy-dispersive X-Ray Analysis

Energy-Dispersive X-ray analysis was performed to determine the elemental composition of the ZnO-TiO₂ nanocomposites and to confirm the successful incorporation of Fe into the nanocomposite. The EDAX spectra for undoped and Fe-doped (FZT₅) nanocomposites are presented in Fig. 5 (a) and (b).

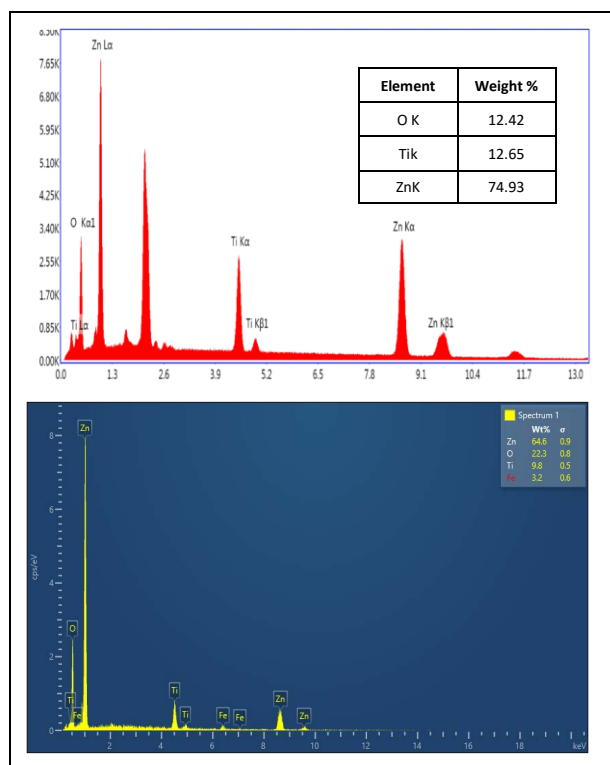


Fig. 5: EDAX spectrum of (a) Undoped (ZT) and (b) Fe-doped (FZT₅) ZnO-TiO₂ nanocomposite

In Fig. 5 (a), the spectrum shows characteristic peaks for Zn, Ti, and O, which are associated with the ZnO and TiO₂ phases, confirming the expected elemental composition of the undoped composite. The presence of these peaks confirms that the ZnO-TiO₂ matrix remains intact and undisturbed when Fe is absent. As shown in

Fig. 5 (b), an additional peak associated with Fe can be clearly seen, indicating the successful incorporation of Fe ions into the composite structure. This peak appears without significant contributions from secondary iron oxide phases like Fe₂O₃ or Fe₃O₄, suggesting effective integration of Fe into the ZnO-TiO₂ framework. The absence of such impurity phases implies that either substitution has occurred where Fe ions replace Zn or Ti within the lattice, or they are well-dispersed as dopants to avoid forming any undesirable secondary phases. Moreover, the EDAX elemental mapping of Fe-doped (FZT₅) nanocomposites demonstrates a consistent distribution of Zn, Ti, O, and Fe throughout the sample. This even spread of elements underscores the effective and uniform integration of Fe within the composite. Such uniform dispersion is essential for maintaining stable electronic and gas-sensing properties across the entire nanocomposite material.

3.5 Fabrication of Thick Films

The initial stages in fabricating thick films involve creating thixotropic pastes and using the screen-printing technique. Essential tools for the screen-printing process include a 200 mesh nylon screen, a printing base, squeegee, glass substrate, and G-clamps. To prepare these thixotropic pastes, the undoped and Fe-doped ZT powders were combined with an ethyl cellulose solution within a mixture of organic solvents like butyl carbitol acetate, butyl cellulose, and turpeneol. The formulation maintained an organic-to-inorganic ratio of 10:90. These prepared pastes were subsequently applied onto glass substrates via screen printing in specific patterns measuring 8 mm × 4 mm. The thick films formed were dried at 80°C using an infrared (IR) lamp. They were then heated to 450°C for 30 minutes in the air. To enable electrical measurements, silver contacts were finally applied on both ends of the films through vacuum evaporation.

Table 2. Thickness evaluation of sensor films using gravimetric analysis

S. No.	Thick Films	Film Thickness (μm)
1	ZT	30
2	FZT ₁	38
3	FZT ₂	28
4	FZT ₃	32
5	FZT ₄	36
6	FZT ₅	34

3.6 Gravimetric Thickness Analysis of Thick Films

This study employed gravimetric thickness analysis to measure the thickness of thick films by using following equation:

$$t = M/\rho A \quad \dots (3)$$

Here, t denotes the film thickness, M represents the mass of the deposited material on the substrate, A is the area of the film, and ρ is the density of the material (Lai *et al.* 2014). The measured thickness values for various thick films are presented in Table 2.

3.7 Electrical I-V Characteristics of Thick Films

The current–voltage (I-V) characteristics of ZT and FZT₁-FZT₅ were evaluated to investigate their electrical response under CO₂ gas exposure. The I-V measurements were conducted at room temperature within a voltage range of -30 V to +30 V, as shown in Fig. 6. All samples exhibited a nonlinear I-V behavior, indicative of hybrid nature of the material characteristics and Schottky-type contact between the sensing film and the electrode interface in both forward and reverse biasing modes. Notably, Fe-doped samples displayed significantly higher current values compared to the undoped ZT sensor, which can be attributed to the enhancement in charge carrier density and improved electrical conductivity due to Fe incorporation into the ZnO-TiO₂ matrix. Among the doped samples, FZT₅ (0.5 mol% Fe) demonstrated the highest current response, suggesting optimized doping concentration for charge transport and gas interaction. The observed increase in current may also be linked to the formation of shallow donor levels, enhanced surface defects, and improved electron mobility arising from controlled lattice distortion and oxygen vacancies introduced by Fe doping.

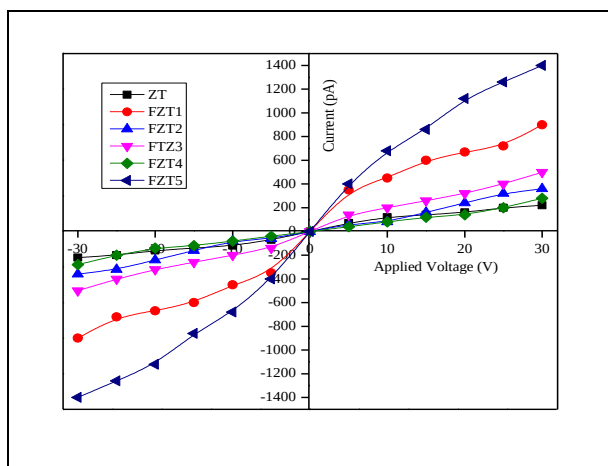


Fig. 6: Variation in I-V response of ZnO-TiO₂ based sensors with increasing Fe doping under CO₂ gas environment

3.8 Gas Sensing Response of ZnO-TiO₂ Thick Films

The gas-sensing performance of the ZT and FZT₁-FZT₅ nanocomposite thick films was evaluated by measuring their response to CO₂ gas at varying

temperatures, as shown in Fig. 7. The gas response (S) was calculated using the standard equation (Pedhekar and Raghuwanshi, 2019):

$$S = \frac{R_{air}}{R_{gas}}, \quad \dots (4)$$

where R_{air} and R_{gas} represent the sensor resistance in air and in the presence of CO₂ gas, respectively. Among the tested thick films, the undoped ZnO-TiO₂ (ZT) nanocomposite exhibited a moderate gas-sensing response, attributed to the heterojunction effect between the ZnO and TiO₂ phases. The presence of well-distributed ZnO and TiO₂ grains facilitated the formation of interfacial charge transfer barriers, which play a crucial role in modulating the sensor response. In contrast, the presence of Fe ions significantly influence the gas-sensing by adding more charge carriers, changing surface defect density, and altering grain boundaries.

The thick film with 0.5 mol% Fe-doping (FZT₅) showed the highest response to CO₂ gas, subsequently followed by FZT₃. The CO₂ gas sensing performances improved in Fe-doped ZnO-TiO₂ nanocomposites due to the structural and electronic changes caused by incorporating Fe ions into their lattice structure, which leads to distortions and defects that create additional oxygen vacancies. These vacancies act as active sites for adsorption, thereby improving gas interaction. Additionally, substituting Fe modifies the electronic structure by increasing the concentration of free charge carriers and refining the kinetics of adsorption and desorption processes. This results in enhanced sensitivity and faster response times.

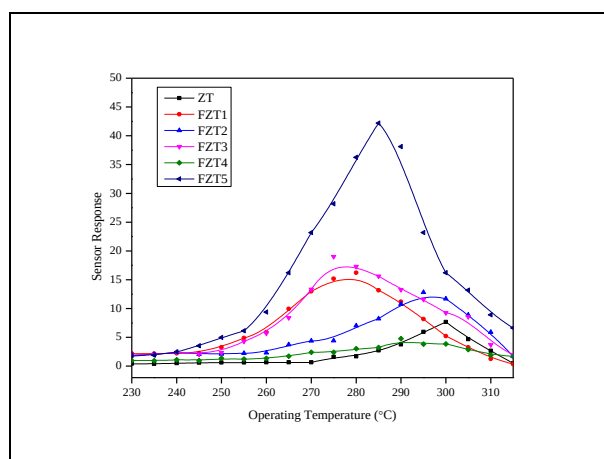


Fig. 7: CO₂ sensing response of ZnO-TiO₂ and Fe-doped ZnO-TiO₂ nanocomposites at varying operating temperature

X-ray diffraction analysis showed that crystallite size decreased from 40.40 nm in ZT to 29.73 nm in FZT₅, along with an increase in dislocation density. The decrease in crystallite size results in a higher density of grain boundaries, providing additional reactive sites for gas adsorption. These combined effects

synergistically enhance the CO₂ sensing performance of the Fe-doped ZnO-TiO₂ nanocomposites, demonstrating their potential as efficient gas sensors. Conversely, lower Fe-doping levels (FZT₁-FZT₂, 0.1-0.2 mol%) exhibited a weaker sensing response, likely due to an insufficient concentration of oxygen vacancies and charge carriers. Moreover, at higher Fe concentrations (>0.5 mol%), excessive doping could lead to carrier recombination effects, thereby reducing sensitivity. Thus, the FZT₅ (0.5 mol% Fe-doped ZnO-TiO₂) nanocomposite exhibited the most promising CO₂ sensing performance, demonstrating higher sensitivity, faster response-recovery times, and improved selectivity at an optimized operating temperature of approximately 280 °C.

3.9 Selectivity of FZT₅ Thick Film

The selectivity of FZT₅ thick film sensor was evaluated against CO₂, LPG, H₂S, and NH₃ gas to determine its preferential gas response, as shown in Fig. 8. Among the gases tested, the FZT₅ sensor demonstrated the highest response (38.26) to CO₂ at 286 ppm, highlighting its strong selectivity for detecting this gas. The FZT₅ thick film exhibits enhanced selectivity, attributed to the increased concentration of oxygen vacancies caused by Fe ions and optimized charge carrier dynamics, which collectively improve the adsorption-desorption interactions with CO₂ molecules. During comparative evaluations, H₂S and NH₃ showed moderate response because of the reducing nature of the gas however LPG shows negligible response, shows the moderate nitration with sensor surface. The 0.5 mol% Fe-doped ZnO-TiO₂ (FZT₅) nanocomposite thick film exhibits enhanced selectivity for CO₂ gas, making it highly suitable for environmental monitoring and industrial applications.

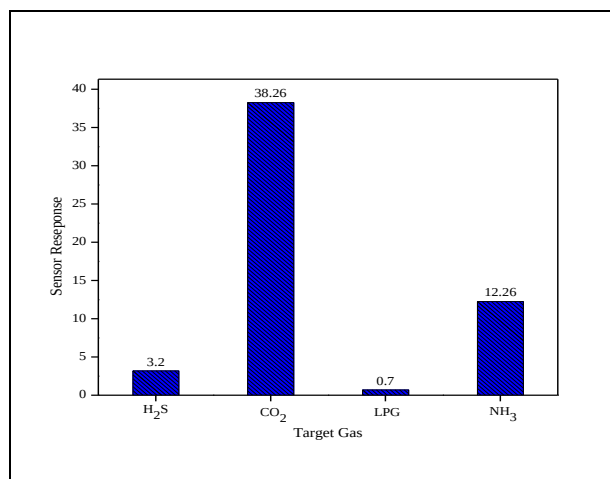


Fig. 8: Selective nature of sensor to CO₂ gas

3.10 Response and Recovery of FZT₅ Thick Film

The CO₂ response and recovery characteristics of the 0.5 mol% Fe-doped ZnO-TiO₂ (FZT₅) thick film

sensor to 286 ppm at of 280°C are depicted in Fig. 9. At an optimal operating temperature around 280°C, the FZT₅ thick film exhibits enhanced sensitivity with quick response time of approximately 10 seconds to 286 ppm of CO₂ gas concentration, attributed to enhanced interactions between CO₂ molecules and active sites of the thick film, such as oxygen vacancies created by Fe doping and the FZT₅ thick film demonstrates recovery of around 50 second suggesting FZT₅ sensor exhibited efficient desorption process for CO₂ from its surface. The rapid response and recovery times highlight the FZT₅ sensor suitability for real-time CO₂ sensing applications where timely detection and reset are essential for precise gas monitoring performance.

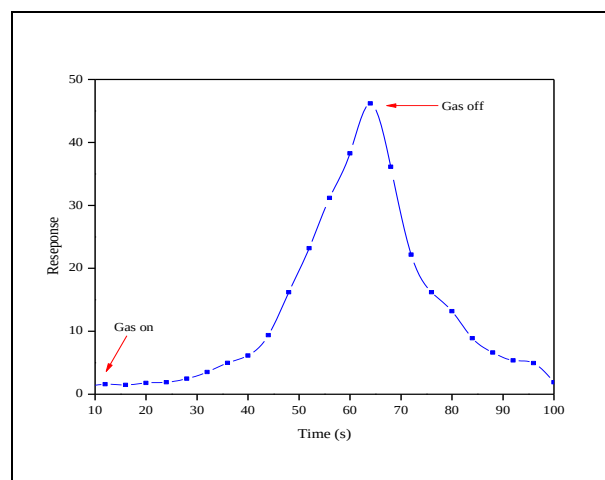
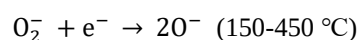
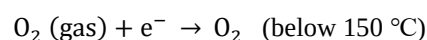


Fig. 9: Response-recovery profile of the sensor

4. DISCUSSION

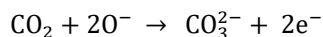
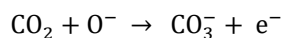
Fe-doped ZnO-TiO₂ nanocomposites (FZT₅) exhibit a gas sensing response to CO₂, primarily controlled by surface-level chemiresistive mechanisms. This involves redox interactions between the target gas and oxygen species adsorbed on the sensor surface. At an operating temperature of 280°C, thermally induced adsorption of oxygen becomes predominant in influencing the sensor's behavior, leading to the creation of ionized forms like O⁻ and O²⁻ on its surface.

Under ambient conditions, oxygen molecules adsorb onto the surface of the nanocomposite and extract electrons from the conduction band, forming negatively charged oxygen ions and establishing an electron depletion layer, which increases the sensor resistance (Khoramshahi *et al.* 2024; Sopiha *et al.* 2021):



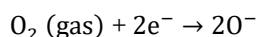
Upon exposure to CO₂ gas at 280°C, the target molecules react with these surface-bound oxygen species, leading to the formation of carbonate

intermediates such as CO_3^- and CO_3^{2-} . These reactions release electrons back into the conduction band, reducing the width of the depletion region and resulting in a measurable decrease in resistance (Saad *et al.* 2024)



Fe^{3+} incorporation into the ZnO-TiO₂ lattice introduces lattice distortions and defect states, which promote the formation of oxygen vacancies (VO). These vacancies serve as active sites for CO₂ adsorption and improve the overall gas-sensing performance by increasing the density of chemisorbed oxygen and enhancing charge carrier mobility. X-ray diffraction analysis confirmed a reduction in crystallite size from 40.40 nm (ZT) to 29.73 nm (FZT₅), along with an increase in dislocation density, which correlates with an enhanced density of grain boundaries that further contribute to surface reactivity.

After CO₂ removal, ambient oxygen molecules re-adsorb onto the nanocomposite surface, again capturing conduction band electrons:



This process restores the original depletion region and resets the sensor's baseline resistance, allowing reproducible sensing cycles. The optimized nanostructure of FZT₅, including increased surface area, active defect sites, and efficient electron transport across the ZnO-TiO₂ interface, facilitates fast adsorption-desorption dynamics, making it highly selective and responsive to CO₂ gas at moderately elevated temperatures.

5. CONCLUSIONS

This study examined the potential of Fe-doped ZnO-TiO₂ nanocomposites as effective and adaptable materials in CO₂ sensing applications. The successful incorporation of Fe into the ZnO-TiO₂ matrix was confirmed by various characterization techniques. Scanning Electron Microscopy images confirmed the uniform distribution of ZnO and TiO₂ phases and revealed well-dispersed Fe dopants. The nanocomposites, particularly the 0.5 mol% Fe-doped sample (FZT₅), exhibited enhanced microstructural and gas-sensing properties. The superior gas-sensing abilities of Fe-doped ZnO-TiO₂ nanocomposites can be credited to their increased surface defect density, elevated charge carrier concentration, and fine-tuned adsorption-desorption kinetics. The study reveals that optimizing doping concentrations and fine-tuning microstructural features lead to significant improvements in both the sensitivity and selectivity of the sensor for detecting CO₂ at a concentration of 286 ppm under an operational temperature of 280°C. These findings indicate that Fe-

doped ZnO-TiO₂ nanocomposites hold considerable potential as materials for developing efficient CO₂ sensors that can perform effectively in both environmental and industrial conditions.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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