

Iron Doped Cobalt Oxide Thin Films for Enhancement of Glucose Sensing Application

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Abstract

In the present study, effect of Fe doping on structural, optical, electrical and glucose sensing properties of nanostructure spinel cubic Co₃O₄ thin films have been depicted by varying 0, 2, 4, 6, 8 and 10 at% Fe doping concentration. The films are prepared by spray pyrolysis technique onto the plain glass substrate taking 350°C pre heated substrate temperature using Co(CH₃COO)₂·4H₂O and FeCl₃ as a source of Co and Fe. XRD analysis explicit spinel cubic structure of Co₃O₄ with lattice parameters $a = b = c = 8.0764 \text{ \AA}$ and average crystallite size 29 nm. 2, 4, 6, 8 and 10 at% Fe introduces average crystallite sizes as 31, 35, 32, 30, and 27 nm indicating maximum sizes of 35 nm for 4 at% Fe, due to large surface area and lowest dislocation density which shows highest glucose sensing performance. UV-vis spectroscopy reveals high transmittances (63% - 95%) in the IR region ($800 \text{ nm} \leq \lambda \leq 1100 \text{ nm}$) and maximum transmittance 95 % is obtained at 4 at% Fe for structural stoichiometry and red shift. Optical band gaps are found between 1.73 eV to 2.21 eV for 0-10 at% Fe respectively due to d-d, s-p and p-d transitions of Co and Fe ions. Carrier concentration is found $5.78 \times 10^{17} \text{ cm}^{-3}$ at 4 at% Fe. Maximum sensing ability is found $2400 \mu\text{A mM}^{-1}$ (24 %) with response time of 2 secs for 4 at% Fe: Co₃O₄ thin films which delineated the suitability of the film for sensor material with high sensing performance.

Keywords: Thin-film; nanostructure; Fe doped Co₃O₄; XRD; glucose sensing

INTRODUCTION

In recent years, nanostructure metal oxides have become a focal point of researchers because of their wide ranging applications in biology and medicine systems including drug delivery, blood glucose monitoring, bio-imaging, cancer and gene therapies, etc. [1-3]. A large number of researchers have extensively studied on transition metal oxides in order to delineated glucose sensing performance. Some transition metal oxide thin films such as Fe₂O₃, MnO₂, Co₃O₄, NiO, TiO₂, SnO₂ etc. are being widely used in glucose sensors due to their advantages of high sensitivity, flexibility and simple manufacturing process [4-6]. In 2015 Meng Zhang studied on glucose detections which are convenient techniques for the diagnosis of diabetes mellitus and require high performance glucose sensors. In 2017 Adawiya J. Haider investigated nanostructured SnO₂ thin film as glucose sensor and found higher response, fast rise and suitable recovery time. Mohamed H. Hassan in 2021 developed nanostructured metal oxides biosensors and observed improve the selectivity and stability. In 2024 Abera Demeke Ambaye developed biosensor of carbon nanostructured materials for glucose detection and observed enhanced analytical performances regarding,

sensitivity, selectivity the limit of detection and reproducibility towards glucose detection. In 2025 Rajaram Rajamohan studied on Au nanoclusters (NCs) enhance glucose biosensors and found high surface area and unique optical properties enable the creation of sensitive, selective devices with low detection limits and rapid response times [7-11].

It is perceive from review of the past literature that nanostructured transition metal oxides play a vital role in the field of glucose sensors where sensing is performed with either catalase or glucose oxidase but they have some limitations as limited operating conditions, short life times, instability, high cost, and frequent maintenance requirements. So, the current research focuses on the formation of nanostructured spinel cubic Co₃O₄ thin films as a function of Fe and role of Fe contents on structural, optical and electrical properties to make suitable for glucose sensor. To best of our concern, no systematic reports have been published on the measurement of structural, optical and electrical parameters of spinel cubic Co₃O₄ thin films as function of Fe impurities for the enhancement of glucose sensing performance. Since Co₃O₄ has more versatile behaviors that are highly dependent on the physical and chemical properties of nanomaterials with optical band gap of 2.0-2.4 eV and p-type charge carrier, so a deep attention has given on the subject of average crystallite size, optical band gap, and electrical conductivity of the films so that they have a good potential in glucose sensors [12-14]. Fe is taken as a dopant element because the ionic radius of Fe³⁺ (0.64 Å) is lower than that of Co²⁺ (1.99 Å) and Co³⁺ (1.89 Å) and so Fe can easily incorporate into Co matrix. However, the presence of Fe as an dopant has influence on structural, optical and electrical properties. Several techniques are used to prepare transition metal oxides thin films such as chemical bath deposition technique [15], spin coating method [16], hydrothermal method [17], spray pyrolysis deposition technique [18] etc. Among these techniques, the spray pyrolysis deposition technique has been chosen as a suitable technique because it has numerous advantages as ease to control deposition parameters, low cost experimental equipment, scope of large area deposition and ability to prepare high quality and small dimensions' nanostructure materials. [19-20].

The main objective of this research is to synthesize a nanostructured Fe doped Co₃O₄ (Fe: Co₃O₄) thin films of various Fe concentration for enhancement of glucose sensing performance. Then comes the point to discuss the structural, optical, and electrical and glucose sensing properties of Fe: Co₃O₄ thin films of 0, 2, 4, 6, 8 and 10 at% Fe doping concentrations. To achieve the research goal, an enzymatic mechanism with the advantages of low cost and simple operation has been presented where glucose is oxidized into gluconolactone and glucose oxidase immobilized on Fe:

Co_3O_4 nanoparticles showing promising ability for the detection of glucose. These characteristics may reveal the suitability of Fe: Co_3O_4 thin films for use in glucose and other biosensor devices.

In view of synthesizing nanostructure Fe doped Co_3O_4 (Fe: Co_3O_4) thin films by spray pyrolysis technique varying Fe doping concentration at 0, 2, 4, 6, 8, and 10 at %, the analytical grade cobalt acetate tetra hydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ (Mark, 99% purity) and Iron Chloride (FeCl_3) (Mark, 98% purity) powder are used as mother precursor for the sources of Co and Fe respectively. Deionized distilled water is used as a solvent. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) and hydrochloric acid (HCl) are used as reagent to control the pH value. The plain glass slide of area $5 \times 2.5 \text{ cm}^2$ with a suitable mask is used as a substrate. In a typical procedure, 0.1 M aqueous solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ mixed with different percentages (0-10 at %) of FeCl_3 powder is prepared into 100 mL double-distilled water, including a few drops of $\text{C}_2\text{H}_5\text{OH}$ and HCl. Solution concentration is kept 0.1 M constant. Mixed solvent is stirred about 1 hour to form a clear homogeneous solution. After that, the solution is filtered and then sprayed through a fine bore in the form of fine droplets onto the pre-heated commercial glass substrates. By spraying the solution onto the cleaned glass substrate at 350°C constant substrate temperature, the films are synthesized. The deposited thin films are allowed to cool at room temperature. The compressed dry air was used as a carrier of gas and gas flow was kept 0.5 bar fixed. Nozzle to substrate distance was 25 cm, the flow rate was 0.5 mL/min, and the deposition time was fixed for 20 min. D-glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and sodium hydroxide (NaOH) were used as precursors for glucose sensitivity measurements. The film preparation process is shown in Fig. 1. Schematically.

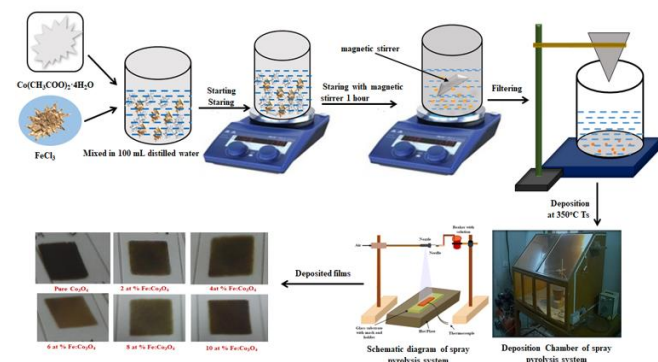


Fig.1. Schematic representations of Co_3O_4 and Fe doped Co_3O_4 thin film synthesis process

II. Characterization techniques

Quantitative analyses of the deposited films have been carried out by field emission scanning electron microscopy (FESEM), energy dispersive X-Ray (EDX) spectroscopy. Structural properties are recorded by using a powder X-ray diffractometer (model: PANalytical Empyrean series 2, using $\text{CuK}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$), with a diffraction angle between 10° to 80° . The crystallite size has been determined from the broadening of corresponding X-ray spectral peaks by using Debye-Scherrer's formula. Optical characterizations of the films are carried out over 200–1100 nm wavelength by a

UV-2600, Pc: UV–VIS–NIR; Shimadzu, double beam spectrophotometer. Electrical measurements are carried out by the four-probe method. Glucose sensitivity was measured by an electrical method.

RESULTS AND DISCUSSION

I. Surface Morphological Analysis

Fig.2. shows the FESEM micrographs with EDX spectra of Co_3O_4 thin film taken at 10,000 magnifications with the scale bar length $1 \mu\text{m}$. and shows nanostructured polycrystalline surface. The micrograph shows the rough surface with porous and polycrystalline nanostructure. The reason to form such surface is for the faster nucleation and growth rates and also rendering a high energy to the source materials for which film become non equilibrium state on the substrate. The surface roughness with high porosity nature is also observed. Which may due to the decrease of solution viscosity, surface tension and vaporization of the organic precursor materials and partially decomposed at the lower substrate temperature (below 400°C). Besides, when the spray droplets collide with the surface of the substrate, they may be dried, and due to this phenomenon, the droplets may not get enough time to spread out on the surface uniformly, and as a result, a rough surface is grown. Porous surface can be beneficial as it allows for faster drying of the crystals reducing the molding together effect which can deteriorate crystal properties. Such surface is favorable for bio sensing applications which are comparable to the prior results [21-22]. The peak for Co and O shown in EDX spectra confirm the formation of Co_3O_4 .

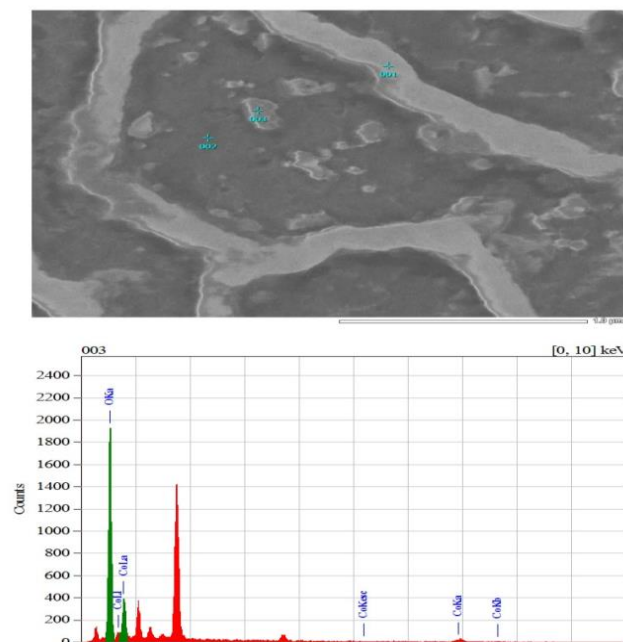


Fig. 2. FESEM with EDX spectra of Co_3O_4 thin films

II. Quantitative analysis

The quantitative elemental percentage ratios of Co_3O_4 and Fe-doped Co_3O_4 (from 0% to 10%) films are evaluated using energy dispersive X-ray spectroscopy (EDX). Different peaks corresponding to Co and O were found in the spectrum which confirmed the Co_3O_4 thin film. For different concentrations of Fe in the solution, there were also Fe peak in the spectra which confirmed the composition of Co, Fe and O in the Fe doped Co_3O_4 thin films. Fig. 3. Shows the quantitative analysis of

the composition of deposited films containing an average atomic percentage of Fe, Co and O and the at % of Co decrease gradually with the rise of at % of Fe which confirm the stoichiometry and homogeneity of the films. [21, 23]. Co₃O₄ film consists of Co and O of about 63.16 at % and 36.84 at % respectively, which are visible by two strong peaks in EDX spectra.

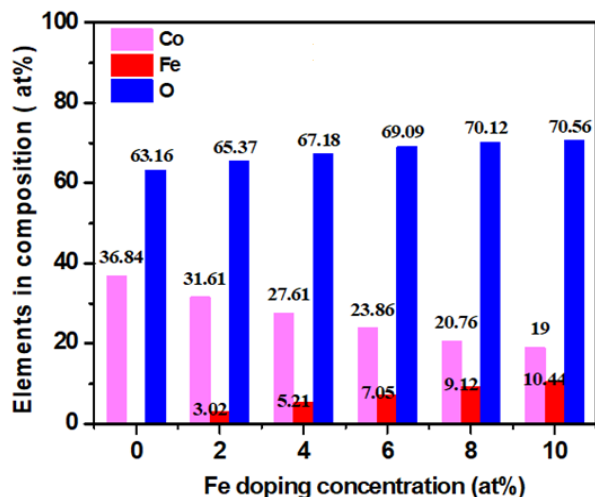


Fig. 3. Quantitative analysis of Fe:Co₃O₄ thin films

III. Structural properties

XRD pattern of Co₃O₄ and Fe doped Co₃O₄ thin films varying with 0, 2, 6, 8 and 10 at% Fe concentrations respectively are displayed in Fig. 4. The preferential orientation of diffracted peaks is observed along (110), (220), (311), (511) and (440) planes at 18.90°, 31.30°, 36.81°, 59.45° and 65.20° diffracted angles respectively for spinel cubic Co₃O₄ which match with JCPDS card no 42-1467 [24]. It is observed that the incorporation of Fe ions into Co₃O₄ matrix strongly modifies the growth of the preferential orientation (311) plane at 36.81° diffracted angle. No other extra peak is found without spinel Co₃O₄ up to 6 at % Fe doping. The reason of such feature is for the systematic presence of Fe³⁺ into the interstitial space of Co²⁺ and Co³⁺ ions without changing the spinel cubic Co₃O₄. At 8 and 10 at % Fe doping a new phase along (024) plane at 49.5° diffraction angle. This peak is formed due to higher doping concentration of Fe ions and formation of Fe₂O₃ which matches with JCPDS card no 24-0072 [25] and the creation of oxygen vacancies caused by the presence of more Fe atoms. The average crystallite size increase up to 4 at % Fe doping then started to decrease. This may due to the super-saturation of Fe ions into the Co₃O₄ matrix indicating a high purity and more stable of the films.

Different structural parameters of Co₃O₄ and 2, 4, 6, 8, and 10 at% Fe doped Co₃O₄ thin films are highlighted in Table 1, which are obtained from preferential orientation (311) plane. Lattice constants have been found to decrease up to 4 at% Fe concentrations and increases from 6 at % to 10 at%. Fe doping. These variations may due to shifting of the peak towards higher angle and effect of different Co and Fe ion sizes which leads to a lattice expansion. These results satisfy with other earlier research works [16, 26]. Dislocation densities decrease up to 4 at% less defects in the system due to the effect of Fe ions that leads to increase the crystallinity. But at 6-10 at% Fe doping the dislocation densities increases

because of decreasing crystallinity and average crystallite size. The variations of texture coefficient with Fe doping concentration express the random orientation of the crystallites for 4 at% Fe having TC_{hkl} = 1.002 (~ 1) which are justified by other research works [24, 27-28] and may a suitable candidate for biosensor developments.

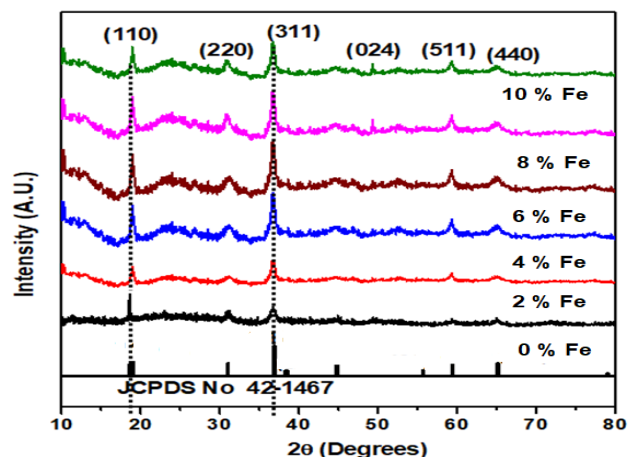


Fig. 4. XRD pattern of Fe:Co₃O₄ thin films at 0-10 at % Fe

Table 1 Structural parameters of Fe: Co₃O₄ thin films

Fe concentration (at%)	Average crystallite size D (nm)	Lattice constant a=b=c (Å)	Dislocation density $\delta = 1/D^2 \times 10^{15}$ (line/m ²)	Texture coefficient TC _{hkl}
0	29	8.0764	1.189	0.953
2	31	8.0513	1.041	0.995
4	35	8.0429	0.816	1.002
6	32	8.0586	0.977	1.113
8	30	8.0653	1.111	1.158
10	27	8.0695	1.372	1.167

IV. Optical properties

The optical transmission spectra of Co₃O₄ and Fe doped Co₃O₄ thin films of different Fe concentration from 0% -10 at % varying with wavelength range from 400 nm to 1100 nm is displayed in Fig. 5. The low percentage of transmittance is found about 10–43% near 400 nm. Thin films exhibited a red shift into the absorption onset at 700 nm. In the vis-region, two sharp absorption edges are observed to lead the charge transfer event of (O²⁻ → Co²⁺) and (O²⁻ → Co³⁺) in Co₃O₄. In the IR region high transmittance is obtained from 63% - 95% highlighted in Fig.5. and maximum transmittance is observed about 95% for 4 at% Fe content. These variation occurs due to absorption of light of the excitation electrons from valence band (VB) to conduction band (CB) and for structural homogeneity. The increase of transmittance may refer to the effects of excess charge carrier for Fe doping that is attributed to the improvement in stoichiometry of the films and it is justified with other research works [17, 20]. The band gap energy shown in Fig. 6. are calculated in the NIR (850-1100nm) region using the Tauc relation, $\alpha = A / hv (hv - E_g)^{1/2}$; where A is a constant, hv is the photon energy and E_g is the optical band gap. The variation of band gap with Fe concentration and film thickness are shown in Fig. 7. The band gaps decrease with increase of 4 at % Fe concentration

and film thickness which may due to incorporation of Fe^{3+} ions into Co_3O_4 and s-p or d-d transition [29-31].

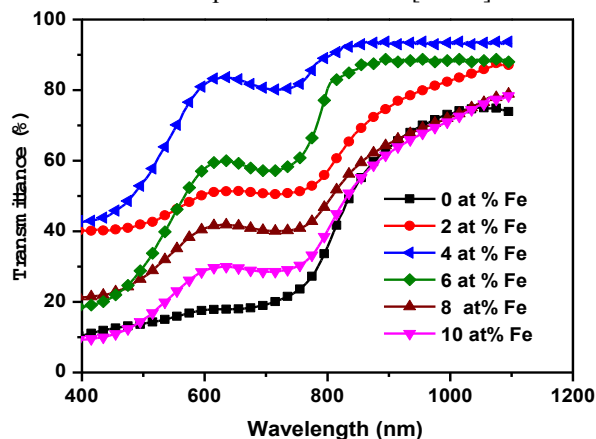


Fig. 5. Transmittance spectra of $\text{Fe}:\text{Co}_3\text{O}_4$ at 0-10at% Fe concentration

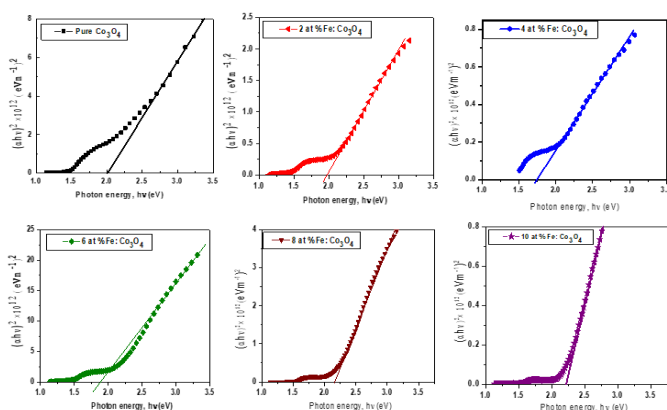


Fig. 6. Band gap of Fe doped Co_3O_4 thin films at 0-10 at % Fe concentration

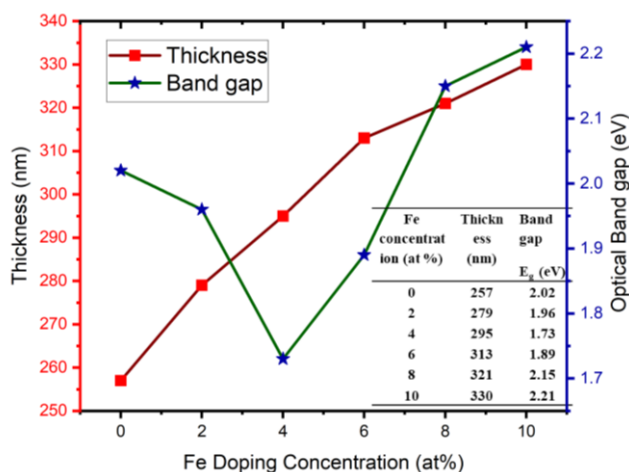


Fig. 7. Variation the Band gap of 0-10 at% Fe doped Co_3O_4 thin films with film thickness

V. Electrical properties

The temperature dependent electrical resistivity of 0-10 at % Fe doped Co_3O_4 thin films are shown in Fig. 8. Variation of temperature is taken from 300 K to 440 K for each film. It is noticed that the resistivity decreases with the rise in temperature. This type of variation indicates the

semiconducting behavior of the films. The decrease in resistivity may be attributed to the increase of the acceptor states associated with the integration of Fe impurities into Co sites of the Co_3O_4 lattice. At high temperature, the resistivity increase with the rise of Fe concentration up to 4 at%. This increase of resistivity may due to the creation of defect as a result of Fe^{3+} either substitution or incorporation into Co_3O_4 lattice. At 6- 10 at % Fe concentration resistivity decrease. The decrease in resistivity may be attributed to the increase of the acceptor states associated with the integration of Fe impurities into Co sites of the Co_3O_4 lattice.

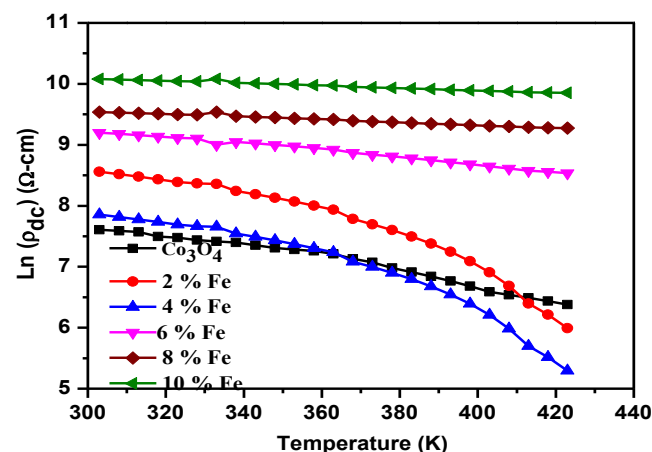


Fig. 8. Resistivity of 0-10 at % Fe doped Co_3O_4 variation with temperature

Table 2 records the electrical parameters of 0, 2, 4,6,8 and 10 at% Fe doped Co_3O_4 thin films. It is observed that the carrier concentration increase with Fe concentration up to 4 at % which may due to the interstitial defects in the Co_3O_4 lattice. Carrier concentration decrease at 6-10 at% Fe doping concentrations that may as a result of crossing the solid solubility limit of Fe ions into Co_3O_4 . Hall mobility decrease in the range of 0-4 at% and increase at 6-10 at % Fe doping which are responsible for number of defects produced in Co_3O_4 by Fe^{3+} incorporation which are compared to other research works [32-34].

Table-2 Electrical parameters of Fe doped Co_3O_4 thin films

Fe concentration (at%)	Resistivity, $\rho(\times 10^4 \Omega\text{-cm})$	Carrier concentration, $n(\times 10^{17} \text{cm}^{-3})$	Hall mobility, $\mu(\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$
0	0.23	2.39	1.81
2	0.19	3.97	1.23
4	0.12	5.78	0.87
6	0.59	4.56	1.23
8	1.67	4.29	1.72
10	1.98	3.18	1.97

VI. Glucose sensing properties

The glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) sensing properties of the prepared thin films has been analyzed by two electrodes as reference and counter electrode and the prepared ($\text{Fe}:\text{Co}_3\text{O}_4$) thin films were as working electrode. In this study, 0.2 M $\text{C}_6\text{H}_{12}\text{O}_6$ (3.62 gm) and 0.2 M NaOH (0.8 gm) were dissolved into 100 ml distilled water and hence NaOH coexists with glucose. A constant voltage of +7 V was applied for the sensitivity (S)

measurement,

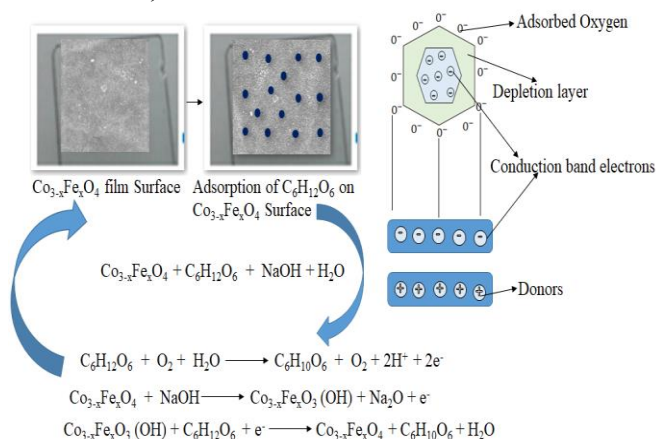


Fig. 9. Glucose sensing mechanism

Glucose-sensing ability of the films was determined using the relation, $S = [(I_a - I_g) / I_g] \times 100$; from without glucose and with glucose; where I_a indicates the current in the air and I_g represents the current-carrying glucose [23,35-36]. Schematic representation of glucose sensing mechanism is shown in Fig. 9. The higher sensing performance is obtained for a high specific surface area of the films. The reason is that the oxidation of glucose is generated being deprotonation of glucose by adsorption onto the film surface. Glucose oxidation generates gluconolactone, and then gluconolactone is further oxidized to glucose. The electrons produced in those reactions are transferred through the film surface. In enhancing sensing ability is a fast electron transfer between Fe doped Co_3O_4 film layer and glucose molecules to improve electron collection. Thus the chemical reaction between glucose and the free air generates free charge carriers (electrons) and increase conductivity which is responsible for increasing sensing ability of the prepared thin films. Sensitivity (S) of 0-10 at % Fe doped Co_3O_4 thin films are shown in Fig. 10.

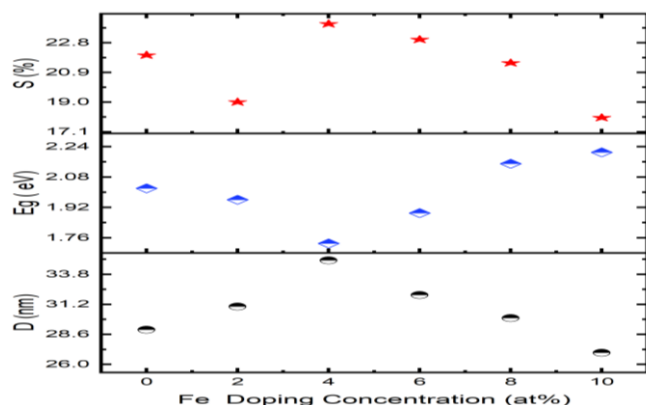


Fig. 10. Sensing properties of 0-10 at % Fe doped Co_3O_4 thin films

Optical band gap (E_g) and average crystallite size (D) of the films greatly effects on the sensing properties. Maximum sensing ability is found $2400 \mu\text{AmM}^{-1}$ (24 %) with response time of 2 secs for 4 at% Fe: Co_3O_4 thin films. Higher crystallite size and lower optical band gap cause enhancing sensing ability. It may because of rapid electron transfer between the Co_3O_4 layer and the substrate to improve electron collection. [37-38]. A comparative study of sensing performance of nanostructured Fe doped Co_3O_4 thin films with other glucose non-enzymatic sensing material of transition

metal oxides is displayed in Table 3. It is observed that the sensing performance of Fe doped Co_3O_4 thin films is much better compared with other oxides materials [39-41] and so our work is comparable to other non-enzymatic glucose sensors and have a prominent advantage such as a wide linear range, reasonable sensitivity, and a quick response time.

Table-3 Comparative study of various non-enzymatic glucose biosensors based on transition metal oxides

Material	Sensitivity (μAmM^{-1})	Response time (sec)	Operating conditions	Synthesis technique	Ref
Co_3O_4 nano needle	4570	8	nonenzymatic alkaline solution. 0.8mM glucose in 0.1M NaOH. Potential +0.55 V	electrochemical methods	[39]
Candy like CuO	1729	30	0.5 mM glucose in 0.1 M NaOH, potential +0.57 V	three electrodes electrochemical method	[40]
Co_3O_4 nanoparticles	743.6	4	nonenzymatic alkaline solution. 5 mM glucose in 0.1M NaOH solution, potential +0.55 V	electrochemical system	[41]
nanostructure Fe doped Co_3O_4 thin films	2400	2	0.2 M $\text{C}_6\text{H}_{12}\text{O}_6$ and 0.2 M NaOH dissolved into 100 ml distilled water. constant voltage +7 Volt	three electrode system electrical method	[present work]

CONCLUSIONS

This work carries out synthesis of nanocrystalline Fe doped Co_3O_4 thin films varying with 0, 2, 4, 6, 8 and 10 at% Fe concentration via a very simple and cost effective spray pyrolysis technique and analysis their characterizations for enhancing glucose sensing performance. Stoichiometry and surface homogeneity of the films is found to increasing with Fe concentration due to the effect charge carrier's which are confirmed from quantitative analysis by EDX spectra. Spinel cubic nanostructures of the films having average crystallite sizes 27-35nm are carried out by XRD analysis. The low percentage of transmittance is found about 10-43% near 400 nm and high transmittance is obtained from 63% - 95% near IR region. Maximum transmittance is observed about 95% for 4 at% Fe content. The variation of these features occur due to spin transition among Fe^{+2} or Fe^{+3} and Co^{+3} or Co^{+2} . Decrease in band gap values represents a red shift at 700 nm. The carrier concentration increase with Fe concentration up to 4 at % and decrease at 6-10 at% due to the effect of crystallite size. Hall mobility decrease in the range of 0-4 at% and increase at 6-10 at % Fe doping which confirm the incorporation of Fe^{3+} into Co_3O_4 matrix. Thus, we concluded that the incorporation of Iron (Fe) into Co_3O_4 containing high transparency, a nonlinear change in direct band gap, large average crystallite size and low resistivity and most importantly, a significant glucose sensing ability for 4 at % Fe doped Co_3O_4 thin film may be a potential material for improvement of glucose sensor. Maximum sensing ability is found $2400 \mu\text{AmM}^{-1}$ with response time of 2 secs for 4 at% Fe doped Co_3O_4 thin films. Higher crystallite size and lower optical band gap cause enhancing sensing ability of the films. This type of film is expected as suitable candidate for glucose bio sensing application.

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Conflict of interest: "The author(s) declare no conflict of interest."

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