



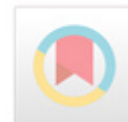
Structural, Optical, and Photoelectrochemical Evaluation of $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ Multilayer Heterostructures for Enhanced Solar-driven Applications

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ABSTRACT

This study presents the fabrication and characterization of a multilayer $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ thin film heterostructure for optoelectronic applications. This heterostructure system was prepared by thermochemical decomposition method. Structural analysis *via* X-ray diffraction confirmed the polycrystalline nature of the films with distinguishable peaks for each constituent layer. The incorporation of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ into the $\text{TiO}_2/\text{SnO}_2$ system led to a reduction in crystallite size and an increase in microstrain, suggesting enhanced lattice distortion and interfacial stress conducive to charge separation. Surface morphology assessed through SEM and AFM revealed uniform grain distribution and improved film compactness in the heterostructure. Optical characterizations conducted by UV-Vis absorption spectroscopy and Tauc analysis revealed that the band gap energy in the pristine SnO and TiO material was 3.20 eV and 3.10 eV, respectively and reduced to 2.25 eV in the resulting composite, which improves the visible light absorption. The refractive index and extinction coefficient were improved in the heterostructured film, and light interaction with matter also improved. Mott-Schottky analysis revealed that all samples are n-type with $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ having a higher flat-band potential (+0.22 V) and lower donor concentration. Such shifts indicate a better band bending and carrier separation. Under illumination, the I-V characteristics showed an increase in photocurrent and a reduction in the dark current in the heterostructure, emphasizing its enhanced photoelectrochemical performance. The overall multilayer $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ system has desirable structural, optical, and electronic characteristics, rendering it a feasible next-generation photovoltaic and photoelectrochemical application.

Keywords: Photoelectrochemical properties; Multilayer oxide semiconductors; Optical band gap engineering; Current-voltage characterization; Surface morphology analysis.

1. INTRODUCTION

Research on the photoactive material technology in renewable energy conversion has become an issue of priority to develop efficient, cost effective and eco-friendly materials due to the growing issues of climate change and energy shortage. Heterojunctions based on semiconductors, and especially metal oxides and chalcogenides, have demonstrated great potential in the area of optoelectronic and photoelectrochemical (PEC) systems because of the tunable band gap, photostability, and synergistic interface charge separation (Fu *et al.* 2022; Hou *et al.* 2022; Danilyuk *et al.* 2022). These heterostructures are successful at increasing charge carrier separation and extending light absorption into the visible spectrum, both of which are important to the efficient harvesting of solar energy (Naujokaitis *et al.* 2018; Jayaraman *et al.* 2021; Ezema *et al.* 2021; Ling *et al.* 2017).

Titanium dioxide (TiO_2) is a highly investigated wide-bandgap semiconductor that exhibits exceptional

photostability, non-toxicity, and electron mobility, which qualify it as an electron transport layer (ETL) and a UV-light-active photocatalyst (Banerjee, 2011; Schneider *et al.* 2014). Its low absorption in the visible region however makes it less efficient in solar driven systems. To overcome this, composite structures with narrow-bandgap semiconductors, such as cadmium sulfide (CdS), zinc-cadmium sulfide ($\text{Zn}_x\text{Cd}_{1-x}\text{S}$), have been investigated to improve light-harvesting efficiency and extend spectral response into the visible spectrum (Laatar *et al.* 2017; Yang *et al.* 2024; Štengl and Králová, 2011).

The zinc cadmium sulfides as solid solutions have a tunable band gap of 2.2 to 2.8 eV, which makes them efficient in harnessing light absorption across the visible light spectrum (Li *et al.* 2013; Ghosh *et al.* 2017). Replacing the CdS lattice with Zn not only modulates the optical bandgap but also can prevent photo-corrosion, a major factor that decreases long-term functionality of these materials (Kang *et al.* 2014). At the same time, tin oxide (SnO_2), a wide-bandgap n-type oxide ($E_g = 3.6$ eV), has also been known to exhibit excellent optical transparency as well as a high electron mobility, thus

qualifying to be a buffer or transport layer in PEC cells (Yusuf *et al.* 2025).

A $\text{TiO}_2/\text{SnO}_2/\text{Zn}_x\text{Cd}_{1-x}\text{S}$ trilayer structure can be designed to increase photoactivity by combining desirable characteristics, i.e. structural stability and extraction of electrons by TiO_2 , carrier mobility and charge transfer at the interface in SnO_2 , and visible-light absorption by $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (Podelinska *et al.* 2025; Wu *et al.* 2020; Chen *et al.* 2019). This structure is projected to enable a type-II band alignment, which is conducive to performing near-theoretical spatial separation of photogenerated electrons and holes, thus minimizing recombination and improving photocurrent generation (Feng *et al.* 2024; Özçelik *et al.* 2016).

In addition, it is possible to combine oxide and chalcogenide layers in coherent multilayer structure to achieve engineering of optical and electronic characteristics via interface properties. Recent experiments have uncovered that these heterostructures can greatly increase spectral absorption, tune flat-band potentials, and access large carrier densities via efficient interface charge transfer and band alignment (Singh *et al.* 2019; Huang *et al.* 2016; Bocarsly *et al.*

2018). The improvements are directly linked to a better PEC performance especially in systems like hydrogen generation and splitting of water. The present work aims at exploring the structural, morphological, optical, and electronic properties of $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructures synthesized by a combination of solution-based methods and thermochemical decomposition.

The development of effective multilayer photoactive heterostructures requires assessment and comparison of the basic physical and chemical characteristics of the elements used. Both TiO_2 and SnO_2 are wide-bandgap, electron-conduction oxides, well characterized by a high degree of structural stability, optical transparency, and electronic conductivity, whereas $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ is a narrow-bandgap, chalcogenide semiconductor that provides superior visible-light absorption and bandgap tunability via Zn/Cd ratio tuning (Sun *et al.* 2015; Singh *et al.* 2012). An in-depth comparison of their structural, optical, and electronic properties is provided in Table 1, which forms a fundamental background to the choice of such materials and justification of their inclusion into the trilayer $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterosystem.

Table 1. Physical and chemical properties of TiO_2 , SnO_2 , and $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$

Property	TiO_2 (Anatase) (Mittal <i>et al.</i> 2018; Dahl <i>et al.</i> 2014; Jolivet <i>et al.</i> 2023)	SnO_2 (Rutile) (Kania <i>et al.</i> 2024; Elsherif <i>et al.</i> 2016; Ahmad <i>et al.</i> 2024)	$\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ (Sun <i>et al.</i> 2015)
Crystal Structure	Tetragonal Anatase	Tetragonal Rutile	Hexagonal + Cubic mixed-phase
Band Gap (Eg)	~3.2 eV	~3.6 eV	~2.3–2.5 eV depending on Zn/Cd ratio
Electrical Conductivity	Moderate (n-type semiconductor)	High (n-type semiconductor)	Good (photoactive semiconductor)
Optical Transparency	Transparent in UV; limited visible light absorption	Transparent in visible; some sub-band tailing	Strong visible light absorption due to narrower band gap
Thermal Stability	Excellent up to ~800°C	High thermal stability	Moderate; can degrade under high illumination without stabilizers
Surface Morphology (Typical)	Nanostructured, spherical grains	Quasi-spherical particles, porous films	Fine grains with high surface area
Refractive Index	~2.5–2.7 in UV range	~2.0–2.1 in UV-visible	~2.4 (varies with Zn/Cd ratio)
Key Applications	Photocatalysis, solar cells, sensors	Transparent conducting oxide, buffer layer	Visible-light absorber, photocatalyst

This paper assesses the crystallinity, grain structure, band gap engineering, and electronic performance of the films through a composite of X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy, and Mott-Schottkey electrochemical data. The goal is to assess the feasibility of these multilayer systems for integration in photoelectronic and solar energy conversion devices. These experimental results are addressed in terms of maximizing interfacial charge transport and broadband light absorption, which is a potential advancement of nanostructured heterojunction design.

2. MATERIALS AND METHODS

2.1 Preparation of Thin Films

TiO_2 , SnO_2 , $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, and $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ thin films were prepared via the Chemical Thermal Decomposition (CTD) technique, which is a scalable, cost-effective technique that yields uniform and crystalline thin films. In the process, precursor solutions are atomized and thermally broken down in contact with a preheated substrate yielding oxide or chalcogenide films via a cascade of redox and thermal processes. The process allows variations in film thickness, stoichiometry,

and microstructure through parameters like precursor concentration, substrate temperature, spraying rate and deposition period. The sequential deposition by this technique was especially beneficial to form the multilayer $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterojunction that can achieve a high interfacial quality and compatibility, and so lead to good electronic and optical properties in photovoltaics.

2.1.1 Preparation of Glass Substrates

Ordinary China glass slides were cut into 2.5 cm $\times$ 2.5 cm squares. These slides served as substrates for thin film deposition due to their high optical transmittance and good adhesion with the deposited films.

Prior to deposition, the glass slides underwent a series of cleaning steps. First, they were washed with water and detergent, followed by ultrasonic cleaning for 10 minutes. Then, the glass substrates were immersed in deionized water and sonicated for another 10 minutes. They were then submerged in 99.99% ethanol and again sonicated for 10 minutes. Finally, they were dried using hot air and special drying paper before being used for film deposition.

2.1.2 Preparation of Spray Solutions

The spray solutions were prepared by dissolving the respective salts in deionized water using a specified molarity, according to the following equation (Achi, 2017):

$$Wt = MWt \times Mt \times \frac{V}{1000} \quad \dots (1)$$

where Wt is required weight to be dissolved (g); MWt is molecular weight of the compound (g/mol); Mt is molarity (mol/L) and V is volume of deionized water (mL).

2.1.2.1 Tin(II) Chloride Solution ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)

Tin(II) chloride solution was prepared from a 99.98% pure reagent from Oxford Lab Chem (UK), at different molarities (0.01 M, 0.02 M, and 0.03 M) and deposition temperatures (325°C, 350°C, and 375°C) in deionized water by stirring on a magnetic stirrer for 30 minutes to ensure complete homogeneity.

2.1.2.2 Zinc Chloride Solution ($\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$)

Tin(II) chloride solutions (0.1 M, 0.05 M) were prepared using 99.98% pure material (HIMEDIA, India) dissolved in deionized water by stirring on a magnetic stirrer for 25 minutes to ensure complete homogeneity.

2.1.2.3 Cadmium Chloride Solution ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$)

Cadmium(II) chloride solutions (0.1 M, 0.05 M) were prepared using 99.98% pure $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (Alfa Aesar, Thermo Fisher Scientific, UK), dissolved in deionized water and stirred on a magnetic stirrer for 25 minutes to ensure complete homogeneity.

2.1.2.4 Thiourea Solution ($\text{CH}_4\text{N}_2\text{S}$)

Thiourea solutions (0.1 M, 0.05 M) were prepared using 99.98% pure thiourea (Alfa Aesar, Thermo Fisher Scientific, UK), dissolved in deionized water and stirred on a magnetic stirrer for 25 minutes to ensure complete homogeneity.

2.1.2.5 Preparation of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$

To prepare $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, 15 mL of the ZnCl_2 solution was mixed with 35 mL of CdCl_2 solution, followed by 50 mL of thiourea solution. The total 100 mL mixture was stirred for 30 seconds to ensure proper mixing.

2.1.2.6 Titanium(III) Chloride Solution ($\text{TiCl}_3 \cdot \text{H}_2\text{O}$)

Titanium(III) chloride solution was prepared from a 99.98% pure TiCl_3 supplied by Merck (Germany). For a 0.05 M solution, 0.95108 g was dissolved in 100 mL deionized water and stirred to ensure complete dissolution and homogeneity.

2.2 Thin Film Deposition

Before spraying, the cleaned glass substrates were placed on a hotplate and preheated for 25 minutes to reach the target deposition temperature. The prepared solution was loaded into the spray chamber, and the spraying process was carried out in pulses: 5 seconds of spraying followed by a 25-second pause, to maintain temperature stability.

Then, the substrates were kept on the hotplate for an additional 25 minutes to complete the chemical reaction and crystallization. Substrates were not removed until they returned to room temperature to avoid cracking or breakage.

2.2.1 Deposition of the Multilayer Structure

Sequential layers were deposited onto a silicon substrate *via* chemical spray pyrolysis (CSP) as follows:

50 mL of TiO_2 precursor solution was deposited to form the TiO_2 layer. A solution containing 7.5 mL

ZnCl₂, 17.5 mL CdCl₂, and 25 mL thiourea (total 50 mL) was sprayed onto the pre-deposited TiO₂ to form the Zn_{0.3}Cd_{0.7}S layer. Finally, 50 mL of SnCl₂ solution was sprayed on top of the Zn_{0.3}Cd_{0.7}S film.

The purpose of sequentially depositing TiO₂, Zn_{0.3}Cd_{0.7}S, and SnO₂ is to achieve a graded band alignment favorable for photovoltaic applications.

2.3 Structural Analysis Using XRD

X-ray diffraction (XRD) analysis was conducted using a Philips PW1730 diffractometer (Holland) equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 30 mA. Diffraction patterns were recorded within the 2θ range of 20° – 80° . The structural parameters of the prepared thin films were extracted using the following equations:

2.3.1 Crystallite Size (D)

The average crystallite size was calculated using the Debye–Scherrer equation (Monshi *et al.* 2012).

$$D = \frac{K\lambda}{\beta \cos \theta} \quad \dots (2)$$

where $K = 0.9$ is the shape factor, $\lambda = 1.5406 \text{ \AA}$ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak in radians, and θ is the Bragg angle.

2.3.2 Dislocation Density (δ)

The dislocation density, representing the density of lattice defects, was evaluated as follows (Serin *et al.* 2006):

$$\delta = \frac{1}{D^2} \quad \dots (3)$$

2.3.3 Number of Crystallite Layers (NL)

The number of crystallite units along the film thickness was calculated as follows (Larbah *et al.* 2016):

$$N_L = \frac{t}{D} \quad \dots (4)$$

where t is the film thickness (typically determined via cross-sectional SEM).

2.3.4 Total Number of Crystallites (No)

The total number of crystallites in the film volume was estimated using the following expression (Serin *et al.* 2006):

$$N_0 = \frac{t}{D^3} \quad \dots (5)$$

2.3.5 Microstrain (ϵ)

The lattice strain in the films was determined using the following equation (Mahammed *et al.* 2023):

$$\epsilon = \frac{\beta \cos \theta}{4} \quad \dots (6)$$

2.4 Surface Morphological Characterization

Surface morphology was examined by scanning electron microscopy (SEM) using a TESCAN MIRA3 system (Czech Republic) operated under high vacuum. The images were used to evaluate grain distribution, surface texture, and the average particle size.

2.5 Optical Characterization and Band Gap Estimation

UV–Vis optical measurements were carried out using a PerkinElmer Lambda double-beam spectrophotometer in the wavelength range 300–900 nm. Based on absorbance and transmittance data, the following optical constants were determined:

2.5.1 Absorption Coefficient (α) (Saad *et al.* 2014)

$$\alpha = \frac{2.303 A}{t} \quad \dots (7)$$

where A is absorbance and t is film thickness (in cm).

2.5.2 Optical Band Gap (E_g) (Haryński *et al.* 2022)

Tauc's relation was employed to determine the optical band gap:

$$(\alpha h\nu)^m = B_0(h\nu - E_g) \quad \dots (8)$$

where $h\nu$ is the photon energy, B_0 is a constant, and $m = 1/2$ for direct transitions (e.g., SnO₂, ZnCdS). Extrapolating the linear region of the Tauc plot to the X-axis yields the band gap.

2.5.3 Extinction Coefficient (k) (Palma *et al.* 2000)

$$k = \frac{\lambda \cdot \alpha}{4\pi} \quad \dots (9)$$

2.5.4 Refractive Index (n) (Urper *et al.* 2023)

Using reflectance (R) and extinction coefficient (k), the refractive index was calculated as:

$$n = \left\{ \left[\left(\frac{1+R}{1-R} \right)^2 - k^2 \right]^{1/2} + \left(\frac{1+R}{1-R} \right) \right\} \quad \dots (10)$$

2.6 Mott–Schottky Analysis and Electronic Properties

Mott–Schottky (M–S) analysis was performed to extract the flat-band potential (V_{fb}) and donor concentration (ND) of the semiconductor films by plotting $1/C^2$ vs applied potential V from capacitance–voltage (C–V) measurements. The analysis was based on the following mathematical models:

2.6.1 Mott–Schottky Equation (Gelderman et al. 2007)

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 e N_D} \left(V - V_{fb} - \frac{kT}{e} \right) \quad \dots (11)$$

where

C : space charge capacitance per unit area (F/cm^2)

ϵ : dielectric constant of the semiconductor

$\epsilon_0 = 8.854 \times 10^{-14} F/cm$: vacuum permittivity

$e = 1.602 \times 10^{-19}$: elementary charge

ND: donor concentration (cm^{-3})

V : applied potential (V)

V_{fb} : flat-band potential (V)

$K = 1.38 \times 10^{-23} J/K$ (Boltzmann constant)

T : absolute temperature (K)

2.6.2 Donor Concentration (ND)

From the linear slope of the $1/C^2$ vs. V plot, the donor concentration was determined by rearranging Equation (11) (Gelderman *et al.* 2007):

$$N_D = \frac{2}{e \epsilon \epsilon_0 \text{slope}} \quad \dots (12)$$

where the slope is the linear coefficient of the M–S plot.

2.6.3 Flat-band Potential (V_{fb})

The flat-band potential was determined from the X-intercept of the linear region of the Mott–Schottky plot (Gelderman *et al.* 2007):

$$N_D = \frac{2}{e \epsilon \epsilon_0 \text{slope}} \quad \dots (13)$$

3. RESULTS AND DISCUSSION

3.1 Structural Analysis of SnO_2 Thin Films

The structural characteristics of SnO_2 thin films synthesized at precursor concentrations of 0.01 M, 0.02 M, and 0.03 M were examined via X-ray diffraction (XRD), as shown in Fig. 1. The diffraction patterns confirm the formation of the tetragonal rutile SnO_2 phase (JCPDS No. 41-1445), with no detectable secondary phases (Shashidhar *et al.* 2013). Prominent reflections were observed at $2\theta \approx 26.8^\circ$, 33.2 – 35.7° , 38.0° , 51.9° , and 54.0° , corresponding to the (110), (101), (200), (211), and (220) planes, respectively. Increasing the precursor concentration enhanced the intensity of these peaks, indicating improved crystallinity.

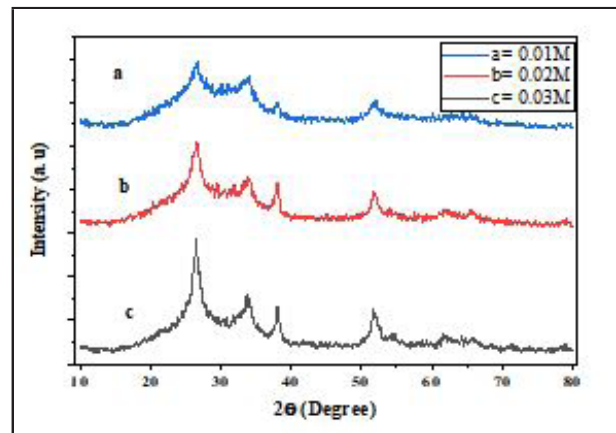


Fig. 1: XRD patterns of SnO_2 thin films synthesized at different precursor concentrations: (a) 0.01 M, (b) 0.02 M and (c) 0.03 M

Crystallite sizes, calculated using the Scherrer equation (2), are summarized in Table 2. Films synthesized at higher concentrations exhibited significantly larger average crystallite sizes rising from ~ 1.7 nm at 0.01 M to ~ 5.5 nm at 0.03 M, attributed to enhanced grain growth and ion availability during deposition.

Microstructural parameters, including microstrain and dislocation density, also showed concentration-dependent trends. The 0.01 M film exhibited the highest microstrain (up to 0.078) and dislocation density (up to 2.18×10^{14} lines/ m^2), consistent with smaller grains and higher defect densities. These values markedly decreased with increasing molarity, reflecting a more ordered crystal structure with fewer lattice imperfections (Kumar and Rao, 2020).

The number of crystallites and estimated film layers further support these findings. Low-concentration films presented a high number of fine crystallites with less dense stacking, while higher molarities yielded thicker

films with fewer, larger grains and better layer coherence. These structural improvements are advantageous for optoelectronic applications, where reduced defect densities and enhanced charge transport are critical (Minami, 2005). Thus, increasing the precursor molarity

effectively improves the crystallinity and microstructural quality of SnO_2 thin films. The 0.03 M sample demonstrated the most favorable structural parameters, making it a promising candidate for multilayered heterostructure fabrication and device integration.

Table 2. Crystallographic and microstructural properties of SnO_2 thin films at different precursor concentrations

Sample	(hkl)	2θ (°)	FWHM (rad)	D (nm)	Microstrain (ϵ)	δ (10^{15} lines/ m^2)	N_0	N_L
SnO_2 / 0.01 M	(110)	26.81	0.00891	0.999	0.03782	1.0	401.45	400.48
	(101)	35.16	0.00495	1.964	0.02058	0.26	52.78	203.65
	(200)	35.75	0.0031	3.158	0.01287	0.1	12.7	126.67
	(220)	54.02	0.02	0.677	0.07762	2.18	1288.08	590.68
SnO_2 / 0.02 M	(110)	26.37	0.00614	1.445	0.02607	0.48	132.53	276.79
	(101)	33.49	0.00442	2.157	0.01846	0.22	39.88	185.48
	(200)	37.96	0.00103	9.738	0.00427	0.01	0.43	41.08
	(211)	51.91	0.00189	6.815	0.00741	0.02	1.26	58.7
SnO_2 / 0.03 M	(110)	26.42	0.00399	2.224	0.01694	0.2	36.35	179.84
	(101)	33.22	0.00487	1.948	0.02038	0.26	54.1	205.33
	(200)	38.04	0.00098	10.28	0.00405	0.01	0.37	38.92
	(211)	51.92	0.00167	7.715	0.00655	0.02	0.87	51.85

3.2 Structural Analysis of TiO_2 Thin Film

The XRD pattern of the TiO_2 thin film (Fig. 2) revealed distinct peaks at $2\theta \approx 25.1^\circ$, 37.8° , and 48.1° , corresponding to the (101), (004), and (200) planes of the anatase phase (JCPDS No. 21-1272) (Hanaor and Sorrell, 2011), with no evidence of rutile or brookite phases. This confirms the formation of a single-phase anatase structure with preferential orientation along the (101) plane.

Crystallite sizes ranged from 12.4 to 15.4 nm across different planes, averaging 14.1 nm (Table 3), indicative of nanocrystalline growth. Microstrain values were low (0.0048–0.0077), as were dislocation densities ($4.21\text{--}6.50 \times 10^{-3} \text{ nm}^{-2}$), signifying a coherent and low-defect structure (Kite *et al.* 2018). The uniformity in crystallite number and layer thickness suggests consistent stacking and interfacial contact, suitable for applications such as photocatalysis and dye-sensitized solar cells (O'Regan and Grätzel, 1991).

3.3 Structural Analysis Results of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ Thin Films

The XRD pattern of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ thin film (Fig. 3) showed major peaks at $2\theta \approx 26.7^\circ$, 44.3° , and 52.1° , attributed to the (002) plane of hexagonal CdS and the (220) and (311) planes of cubic ZnS, respectively (Duan *et al.* 2018). These results confirm the formation of a dual-phase $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ solid solution with mixed crystallographic characteristics.

Crystallite sizes ranged from 4.2 to 10.5 nm, with an average of ~ 7.1 nm (Table 4). The broadness of higher-angle peaks suggests lattice disorder and grain size anisotropy (Mukherjee *et al.* 2015). Moderate microstrain (0.0062–0.0086) and dislocation densities ($0.91\text{--}5.67 \times 10^{-2} \text{ nm}^{-2}$) are consistent with strain induced by lattice substitution between Cd^{2+} and Zn^{2+} (Kumar *et al.* 2017). The film exhibits a multilayered structure (9–24 layers), reflecting dense stacking and good grain connectivity. These features support its use as an efficient light absorber in photoactive heterojunctions (Kumar and Tiwary, 2021).

3.4 Structural Analysis of the TiO₂/SnO₂/Zn_{0.3}Cd_{0.7}S Heterostructure

The XRD pattern of the trilayer TiO₂/SnO₂/Zn_{0.3}Cd_{0.7}S heterostructure (Fig. 4) revealed a superposition of peaks corresponding to the (110), (101), (200), and (211) planes of SnO₂, with overlapping contributions from TiO₂ and Zn0.3Cd_{0.7}S layers. The retention of characteristic peaks without secondary phases indicates successful integration of the three constituents into a coherent multilayer system.

Crystallite sizes in the composite ranged from ~2.15 to ~6.02 nm (Table 5), with an average of ~3.93 nm smaller than TiO₂ alone but within the range of SnO₂ and ZnCdS films. This suggests interfacial constraint on grain growth. Microstrain and dislocation densities were moderate, indicating balanced lattice accommodation across layers. The number of crystallites and film layers confirm dense stacking and interfacial continuity. The composite exhibits structural synergy, preserving individual film characteristics while forming a stable heterojunction suitable for optoelectronic and photovoltaic applications.

3.5 SEM Analysis of SnO₂ Thin Films

The surface morphology of SnO₂ thin films deposited at varying conditions, 0.01 M (Fig. 5a), 0.02 M (Fig. 5b), and 0.03 M (Fig. 5c) was examined using scanning electron microscopy (SEM) at 50,000× magnification. All micrographs reveal a uniformly distributed nanoparticulate structure, characteristic of polycrystalline SnO₂ grown via solution-based or thermal deposition routes. The grains are spherical to quasi-spherical in shape, with distinct boundaries and slight agglomeration in localized regions.

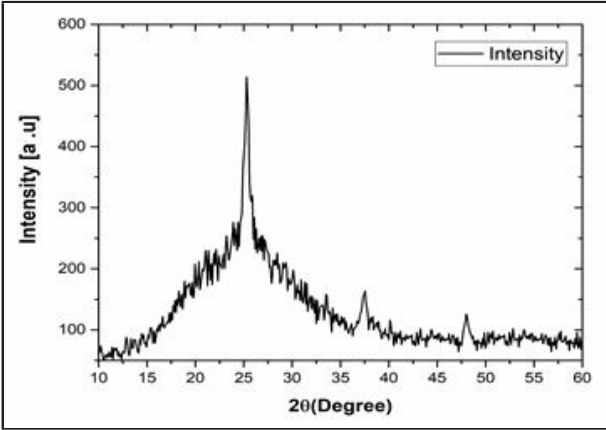


Fig. 2: XRD patterns of TiO2 thin film

Table 3. Crystallographic and microstructural properties of TiO₂ thin films

Sample	(hkl)	2θ (°)	FWHM (rad)	D (nm)	Microstrain (ε)	δ (10 ¹⁵ lines/m ²)	N ₀ (×10 ¹¹)	N _L
TiO2	(101)	25.1	0.0119	12.4	0.0077	6.5	5.2	8
	(004)	37.8	0.0096	15.4	0.0062	4.21	5.2	6
	(200)	48.1	0.0104	14.6	0.0048	4.69	5.2	7

Table 4. Crystallographic and microstructural properties of Zn_{0.3}Cd_{0.7}S thin film

(hkl)	2θ (°)	FWHM (rad)	D (nm)	Micro strain (ε)	δ (1016 lines/m ²)	N ₀ (× 10 ¹²)	NL
(002)	26.7	0.00933	10.5	0.0071	0.91	1.3	9
(220)	44.3	0.01387	6.7	0.0062	2.23	1.3	15
(311)	52.1	0.02453	4.2	0.0086	5.67	1.3	24

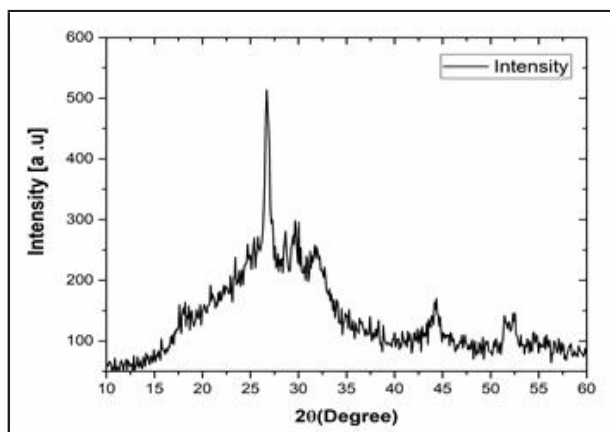


Fig. 3: XRD patterns of Zn_{0.3}Cd_{0.7}S thin film

Quantitative measurements annotated on the micrographs indicate particle diameters ranging between ~26.8 nm and ~62.5 nm, with most values falling between 35 nm and 46 nm. This size range is consistent across the three SEM fields, suggesting homogeneous grain distribution and good film coverage. The moderate variation in particle size may reflect localized differences in nucleation rates during deposition or subsequent grain coalescence during post-annealing (Shashidhar, 2013).

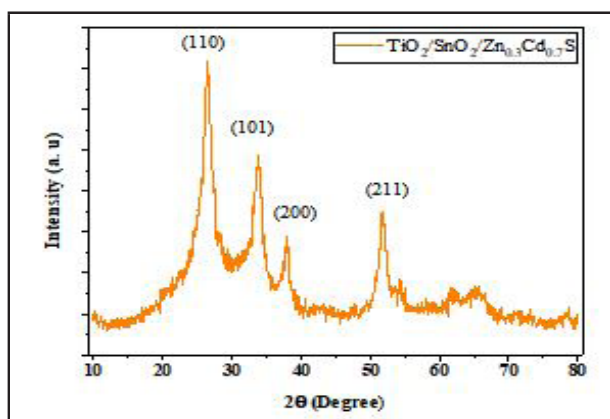


Fig. 4: XRD pattern of TiO₂/SnO₂/ Zn_{0.3}Cd_{0.7}S heterostructure

From a microstructural standpoint, the SnO₂ films display a porous morphology with interconnected nanograins and intergranular voids, which may facilitate gas diffusion or interfacial interaction in electronic or sensing applications (Han *et al.* 2019). The observed particle sizes are in good agreement with XRD-derived crystallite sizes, particularly the average value of ~5.5 nm obtained for the 0.03 M sample using the Scherrer formula. The discrepancy between SEM-observed particle size and XRD crystallite size can be attributed

to the presence of polycrystalline agglomerates, wherein several crystallites coalesce into a single nanoparticle (Khoshkhoo *et al.* 2013).

3.6 SEM Analysis of TiO₂ Thin Film

The surface morphology of the TiO₂ thin film was examined using SEM (Fig. 6). The micrograph reveals a densely packed nanoparticulate structure, with visible surface roughness and well-developed granular texture across the observed field. The nanoparticles appear spherical to sub-spherical, closely interconnected with minimal interparticle voids, indicating a compact film topology.

Grain size estimations annotated on the image range from 31.26 nm to 55.82 nm, with frequent measurements near 40–50 nm, including values of 40.19, 42.43, 49.13, 51.36, and 53.59 nm. This distribution suggests an average particle size in the range ~45 ± 8 nm, larger than the crystallite size (~14.1 nm) calculated from XRD data. This difference is attributed to the polycrystalline nature of TiO₂ grains. Each visible grain likely comprises multiple smaller crystallites aggregated into secondary particles.

Compared to SnO₂ films, the TiO₂ film displays a more compact and continuous morphology, with less porosity and larger aggregates, which is consistent with known tendency of the anatase phase to form larger coherent domains upon annealing (Mathews *et al.* 2009). The absence of deep voids or surface cracks confirms a mechanically robust microstructure, potentially favorable for photocatalytic or photovoltaic applications where surface integrity and interface uniformity are essential (Kim *et al.* 2013).

3.7 SEM Analysis of TiO₂/SnO₂/Zn_{0.3}Cd_{0.7}S Composite Thin Film

The morphology of the multilayer TiO₂/SnO₂/Zn_{0.3}Cd_{0.7}S heterostructure was investigated by SEM (Fig. 7). The microstructure displays a densely packed agglomeration of nanoparticles with a generally spherical morphology and moderate size uniformity. The surface appears compact, with occasional loosely arranged clusters, which likely results from multilayer deposition and partial grain boundary coalescence between the stacked oxide and chalcogenide layers.

Grain size measurements from the micrograph reveal particle diameters in the range 29.03 to 40.19 nm, with intermediate values such as 33.50 nm, 35.73 nm, and 37.96 nm. These values suggest a mean particle size around 34–36 nm, which is consistent with the trend observed in the constituent layers. Compared to

the SEM of individual films, the average grain size of the composite is slightly reduced relative to TiO_2 (~45 nm), and slightly more uniform than SnO_2 (~40 nm) and $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ (~30 nm, if estimated similarly). This suggests that interfacial strain and constrained nucleation during the layered growth process may limit grain expansion, thereby stabilizing smaller but coherent nanostructures.

The composite surface has a good balance between the grain connectivity and considered high-level surface porosity which suggests a proper level of layer integration without big empty spaces and delamination. This type of morphology is well suited to applications where high efficiency charge separation and vertical charge transfer is needed, e.g. solar cells, PEC systems. The controlled particle size and relatively high agglomeration density can also improve the interfacial contact of TiO_2 (ETL)/ SnO_2 (buffer)/ ZnCdS (absorber) layers.

3.8 UV-vis Spectroscopy Analysis

The optical properties of single thin films TiO_2 , SnO_2 , and $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$; and the heterostructure of $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ were determined by UV-Visible spectroscopy. The respective absorption spectra are illustrated in Fig. 8.

The TiO_2 film demonstrates a sharp absorption edge around 380–390 nm, which corresponds to a band gap of ~3.2 eV, typical of the anatase phase. This abrupt absorption indicates minimal sub-bandgap states and high phase purity, as confirmed by XRD and SEM analyses. The UV-selective behavior of TiO_2 limits its activity under visible illumination, but it serves effectively as an ETL due to its conduction band alignment and electron mobility.

Table 5. Crystallographic and microstructural properties of $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$

Sample	(hkl)	2θ (°)	FWHM (rad)	D (nm)	Microstrain (ϵ)	δ (10^{15} lines/m ²)	N_0 ($\times 10^{11}$)	NL
$\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$	(110)	26.46366	0.00348	2.34231	0.01480	0.18227	31.12640	170.77185
	(101)	33.39566	0.00387	2.14504	0.01616	0.21734	40.52807	186.47701
	(200)	37.90240	0.00140	6.01707	0.00576	0.02762	1.83614	66.47758
	(211)	51.82762	0.00169	5.23077	0.00663	0.03655	2.79488	76.47061

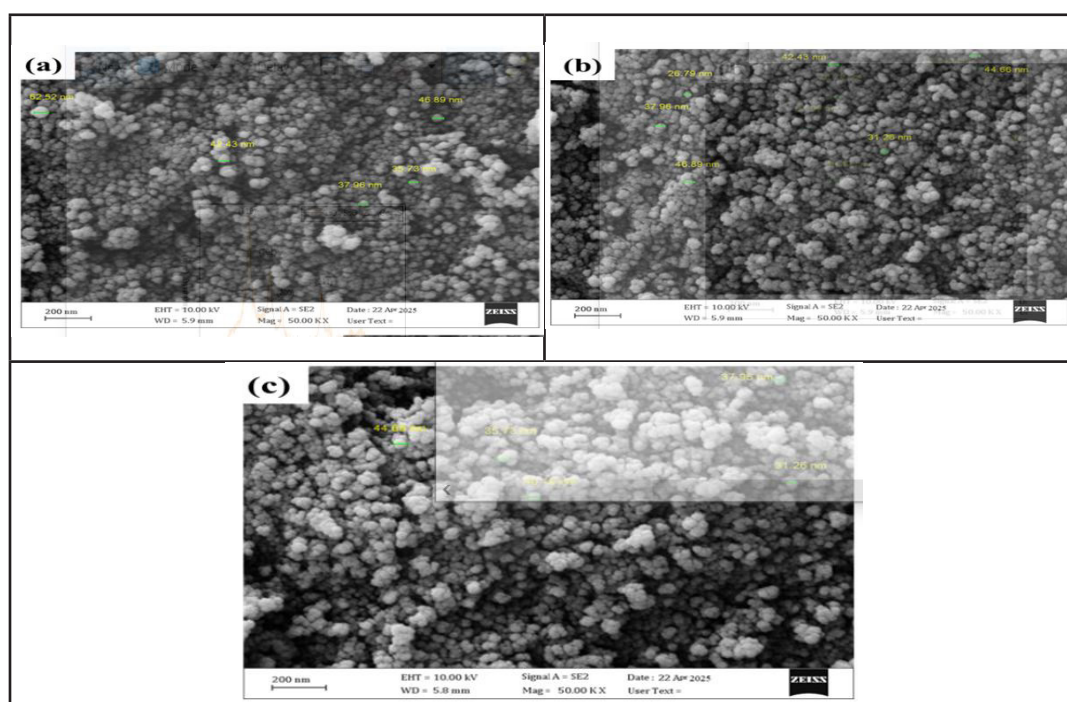


Fig. 5. SEM images of SnO_2 thin films synthesized at different precursor molarities: (a) 0.01 M, (b) 0.02 M and (c) 0.03 M

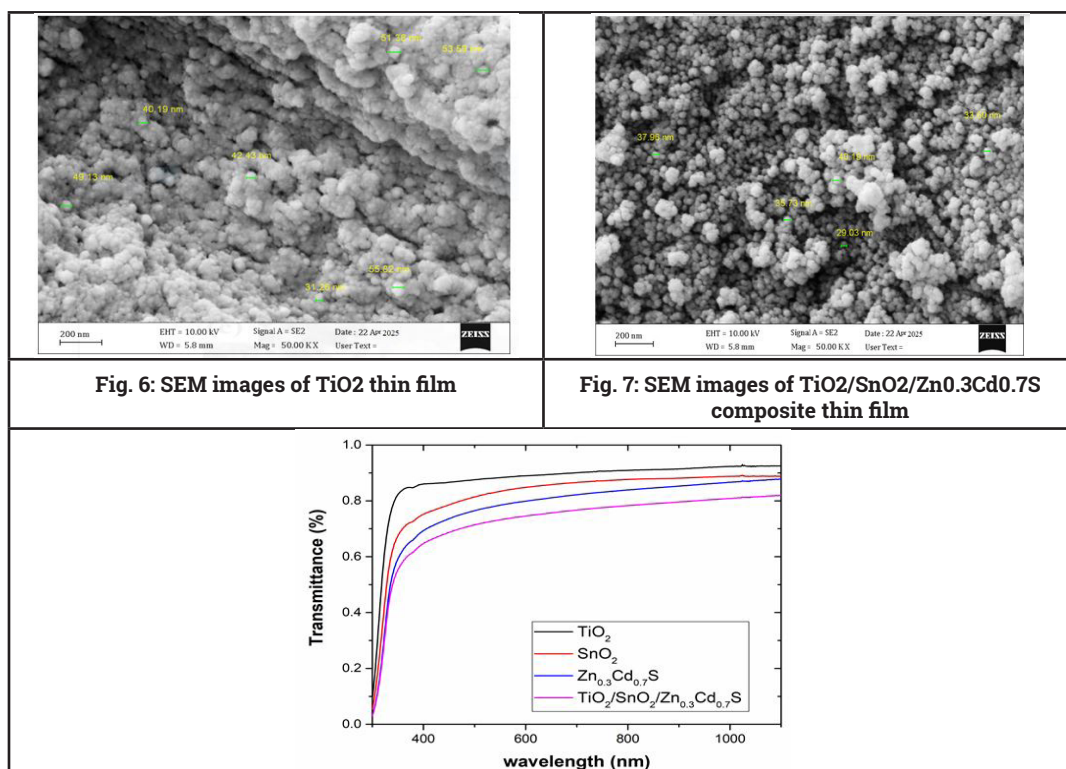


Fig. 8: Optical transmittance spectra of TiO_2 , SnO_2 , $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, and $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ thin films

The SnO_2 film exhibits a broader absorption onset compared to TiO_2 , with spectral extension toward ~ 420 nm. This behavior is attributed to a slightly narrower band gap (~ 3.6 – 3.8 eV) and the presence of shallow defect states, likely due to oxygen vacancies or lattice disorder (Yang et al. 2017). The broader tail in the absorption spectrum is consistent with the microstrain observed in XRD and the porous morphology revealed by SEM.

In contrast, the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ film shows strong absorption in the visible region, with a steep rise beginning around 500 nm, extending up to ~ 650 nm. This behavior reflects a significantly narrower band gap, typically between 2.3–2.5 eV, depending on the Zn/Cd ratio. The high visible-light absorption makes ZnCdS an ideal photoactive top layer in heterostructure assemblies. The smooth, extended absorption profile also indicates a uniform band structure with minimal mid-gap trap states, which is consistent with the polycrystalline but continuous morphology observed under SEM (Wei et al. 2022).

The absorption spectrum of the $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructure demonstrates a combined optical response from all three layers. While retaining the high-energy UV absorption edge from the TiO_2 and SnO_2 layers, the heterostructure also shows a significant broadening of absorption into the visible

region, clearly influenced by the ZnCdS top layer. The synergistic enhancement of absorption across a wider spectral range confirms the benefit of the trilayer design, enabling improved solar energy utilization. The extended absorption also reflects the successful retention of optical characteristics from each layer, with no signs of parasitic absorption or interfacial degradation.

From a structural–optical correlation perspective, the enhanced absorption of the heterostructure aligns well with the intermediate crystallite sizes and modest surface roughness observed by XRD and SEM. The layered configuration and band gap tailoring allow for gradual energy level alignment, facilitating light absorption, exciton separation, and charge transfer across interfaces.

3.9 Absorption Coefficient Analysis

The variation of the absorption coefficient (α) with photon energy for the fabricated thin films is illustrated in Fig. 9. The data provide critical insight into the light absorption capabilities and band structure characteristics of the individual semiconducting layers and their composite.

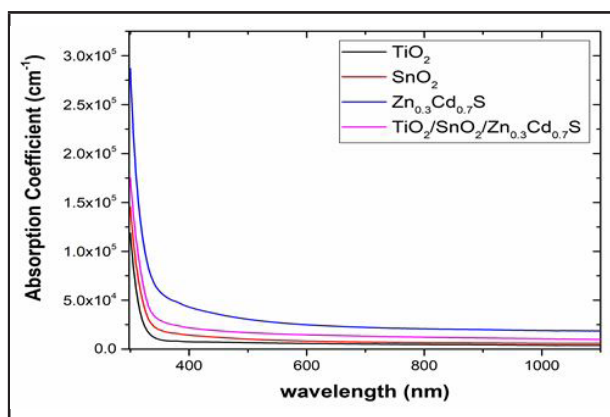


Fig. 9: Absorption coefficient spectra of TiO_2 , SnO_2 , $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, and $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ thin films

As shown above, the ternary sulfide $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ exhibits a distinct and broad absorption profile within the visible region, with a steep rise in α values commencing around 2.4 eV. This behavior is indicative of a narrower band gap, which can be attributed to the solid solution nature of the material, where the partial substitution of Zn^{2+} for Cd^{2+} modulates the electronic band structure. The gradual increase in α and the smooth absorption onset reflect the semiconducting behavior and high optical activity of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, making it an excellent candidate for visible-light-driven applications such as solar energy conversion and photocatalysis.

The TiO_2 film shows a sharp absorption edge near 3.2 eV, consistent with the direct transition of anatase-phase TiO_2 (Manole *et al.* 2013). SnO_2 exhibits a similar UV-absorption profile but with slightly broader absorption, which may be ascribed to tail states induced by oxygen vacancies or other intrinsic defects (Mandal *et al.* 2024). Importantly, the $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ hybrid structure reveals a red-shifted absorption edge extending into the visible region, compared to the binary oxide films. This shift suggests successful spectral broadening due to the inclusion of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ as a visible-light sensitizer.

The broader absorption range observed for the heterostructure implies enhanced photon harvesting capabilities, which is a crucial factor for improving photocatalytic or photovoltaic efficiency (Hadke *et al.* 2022). This enhancement is directly attributable to the synergistic integration of the wide-bandgap oxides with the visible-responsive ZnCdS layer. The absorption coefficient behavior strongly supports the formation of an optically active heterojunction with complementary light absorption properties.

3.10 Optical Band Gap Analysis

The optical band gaps of the individual and composite materials were estimated using Tauc plots derived from the UV-Vis absorption spectra (Fig. 10). These plots, which are based on the Tauc relation for direct allowed transitions, enable the determination of the optical band gap energy (E_g) by extrapolating the linear portion of the plot to the X-axis, where $(\alpha h\nu)^2 = 0$.

For TiO_2 , the Tauc plot exhibits a characteristic sharp absorption edge with a nearly linear rise in the $(\alpha h\nu)^2$ vs $h\nu$ curve. The linear extrapolation of this region intersects the energy axis at approximately 3.20 eV, which is consistent with the reported band gap for anatase-phase TiO_2 (Fujisawa *et al.* 2017). This wide band gap places TiO_2 in the UV-responsive region and limits its absorption capacity under visible light, which is a known constraint in applications such as photocatalysis or photoelectrochemical conversion.

The Tauc plot for SnO_2 shows a similar profile to that of TiO_2 but with a slightly larger extrapolated band gap of around 3.38 eV. The value is consistent with a well-understood large wide band gap of SnO_2 which is associated with its electronic structure and low density-of-states profile at the conduction band edge (Selvakumari *et al.* 2017). SnO_2 has desirable electrical characteristics and chemical stability, but it is optically inactive to visible electromagnetic radiation, limiting the feasibility of using it by itself in solar-powered devices.

Contrastingly, the Tauc plot shows a significantly reduced band gap in the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ semiconductor. The linear section of the curve meets the photon energy axis close to 2.37 eV, reflecting a high redness relative to the oxide analogs. This reduction in the band gap occurs due to increased level of cadmium in the solid solution and effectively tunes the energy between that of ZnS and CdS (Devadoss *et al.* 2021). The band gap observed is beneficial in terms of harvesting visible light, and is a hallmark of II-VI semiconductor alloys with adjustable optoelectronic characteristics.

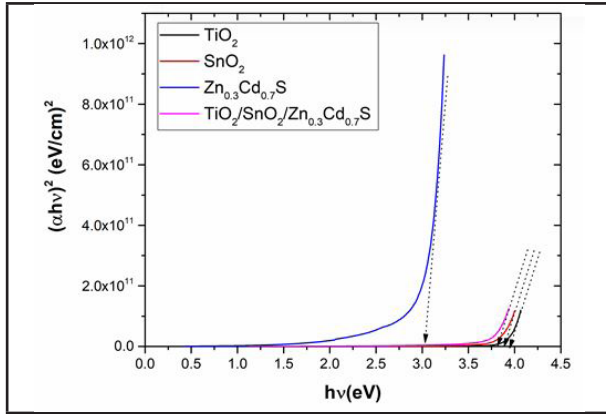


Fig. 10: Tauc plots of TiO_2 , SnO_2 , $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, and $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructures

The hybrid optical behavior of the composite $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ is depicted by the Tauc plot (Fig. 10). The absorption edge of the composite is moved to lower photon energy than that of TiO_2 and SnO_2 alone with an approximate band gap of 2.70 eV. This decrease shows that the incorporation of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ material into the oxide lattice was successful, which allowed modifying the band gap at the formation of heterojunction. The redshifted band edge increases the absorption capacity of the composite within the visible range, which extends better photon exploitation and greater capacity of photoactive outputs.

Taken together, the Tauc plot analysis supports a view of the adaption of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ in the engineering of optical band structure of the $\text{SnO}_2/\text{TiO}_2$ matrix. The formation of the ternary composite results in the formation of intermediate energy states and the improvement of interfacial charge transfer, which is desirable in such applications that involve high visible-light activity, including photocatalysis, solar cells, and optoelectronic devices. The capability to design the band gap through composition and layering techniques attests to the feasibility of this composite strategy on the development of advanced functional materials.

3.11 Refractive Index Analysis

The spectrum of the refractive index of TiO_2 (Fig. 11) demonstrates its high optical activity in the ultraviolet band due to its heavy dielectric constant and dense electronic structure. TiO_2 has a refractive index peak at lower photon energy which smoothly reduces as the photon energy increases (Kang *et al.* 2018). This is the characteristic dispersion behavior of dielectric materials where dispersion is determined by interband electronic transitions (Kasap *et al.* 2020). Strong photon-matter interactions are related to high values of refractive

index, making TiO_2 very effective as an anti-reflective coating and photocatalyst. The original sharp peak in the refractive index indicates a large density of states around the valence band maximum, enabling highly efficient absorption and optical response at the UV frequency.

Comparatively, SnO_2 exhibits a slightly lower curve of the refractive index over the same region of the spectrum. The reason behind this difference is because it has a relatively wider band gap and low polarizability as opposed to TiO_2 . SnO_2 also shows a decreasing refractive index with photon energy, but less steep than in the case of ZnO , suggesting a less significant difference in electronic transitions (Zulfqar *et al.* 2017). SnO_2 remains transparent in the visible range, but the smaller refractive index means that it can be less capable of light confinement compared to TiO_2 . However, the optoelectronic applications of SnO_2 are frequently preferred because of its high carrier mobility and its transparency, which counteract its reduced optical density.

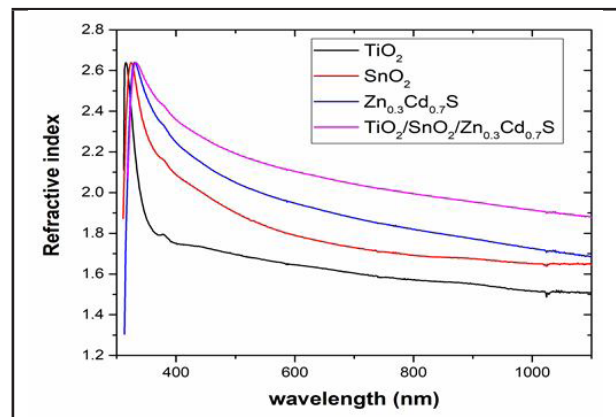


Fig. 11: Variation of refractive index as a function of wavelength for individual and multilayer thin films: TiO_2 , SnO_2 , $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, and $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructure

The optical properties of the ternary chalcogenide $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ are markedly different, with an intermediate range of high initial refractive index and a strong decrease as the photon energy increases. The higher refractive index at low energy region is attributed to the narrower bandgap and the high polarizability of the Cd-rich sulfide matrix (Iqbal *et al.* 2022). This substance enables strong optical transitions at low photon energies, which make light matter interactions significant. The trend is explained by the localized electronic states and increased polarizability due to the heavy-metal elements (Cd and Zn) (Mazumder *et al.* 2024). This makes $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ especially useful where there is a need to achieve high absorption and refractive control within visible light, e.g., in visible light photocatalysis and

photodetector applications.

$\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ has a composite refractive index profile showing all three required constituents reflecting in the profile. This spectrum retains high refractive index values even in the low energy photon range and demonstrates a smoother decrease than each of the individual oxides. This improvement is attributed to the synergetic effect of the interface interactions and enhanced density of interband states due to the layered layout. The polarizability of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ combined with structural integrity in the oxide layers enhances the optical density of the composite. Additionally, the extension of the refractive index spectrum implies a wider range of light absorption, further affirming the potential adaptation of this heterostructure in multi-functional optoelectronic applications, such as solar cells and in-hybrid photocatalysts. The resulting overall optical performance therefore upholds the postulation that the composite architecture increases the efficiency of light management by promoting better photon capture and electronic transition dynamics.

3.12 Current–voltage (I–V) Characteristics Analysis

The current-voltage (I-V) characteristics are of primary diagnostics used to analyze the electrical behavior of semiconducting materials under dark and illuminated conditions. These are important properties particularly when evaluating its potential as a material to convert sunlight to electricity, and they can provide ideas about the photoresponse efficiency, charge carrier dynamics and junction behavior. Comparative I-V analyses was also carried out in this study in two configurations, in a pristine of SnO_2 thin film and a ternary $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructure in ambient light and dark situations.

Fig. 12 displays the I-V response of the SnO_2 thin film, a wide bandgap n-type semiconductor traditionally employed in transparent conducting applications. Under dark conditions, the I-V curve remains nearly linear with low current levels, indicative of the intrinsic resistive nature of the film and the absence of thermally generated carriers. Upon illumination, a marginal increase in current is observed across the voltage range. This limited photocurrent suggests a low density of photogenerated carriers and/or inefficient separation due to the lack of internal electric fields or heterojunction interfaces. The absence of significant rectification further implies minimal built-in potential, which diminishes the material's ability to efficiently drive carrier separation (Wang *et al.* 2009). Hence, while SnO_2 exhibits a weak photoconductive response, its isolated performance is insufficient for effective photovoltaic applications.

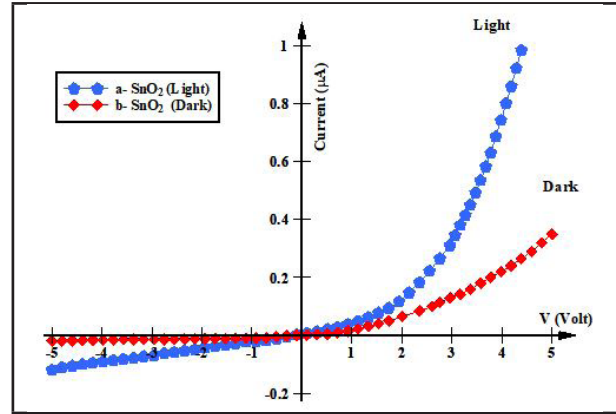


Fig. 12: Current–voltage (I–V) characteristics of SnO_2 thin film measured under dark and illuminated conditions

In contrast, Fig. 13 illustrates the I-V behavior of the $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructure, which exhibits pronounced rectifying characteristics and enhanced photocurrent under illumination. The light I-V curve reveals a strongly nonlinear response with a steep rise in current at forward bias, far exceeding that observed in the dark. This distinct enhancement in photocurrent underscores the significant improvement in photoelectric conversion, highlighting the successful integration of functional materials with complementary properties. The dark current remains low, confirming that the junction effectively suppresses leakage or thermally activated charge flow.

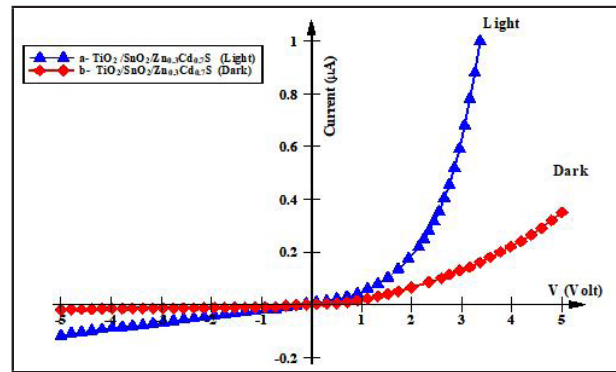


Fig. 13: Current–Voltage (I–V) characteristics of $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ thin film measured under dark and illuminated conditions

The improvement in photoresponse can be attributed to multiple synergistic effects within the heterostructure. TiO_2 , serving as the top layer, provides structural stability and acts as a UV-active layer. SnO_2 , with slightly higher conductivity and a suitable conduction band level, facilitates electron transport while acting as an intermediate layer. $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$, with a narrower band

gap and visible-light sensitivity, significantly broadens the spectral absorption range of the system. This band alignment is expected to form a cascade-type or type-II heterojunction, where the conduction band minima and valence band maxima are staggered, thereby enabling spatial separation of electrons and holes across the different layers.

From a solar cell perspective, such a configuration is highly advantageous. The built-in electric field at each interface aids in the dissociation of excitons (electron-hole pairs) and promotes unidirectional transport of carriers (electrons toward the anode and holes toward the cathode) minimizing recombination losses. Moreover, the low dark current indicates minimal reverse leakage, which improves the open-circuit voltage (V_{oc}) and overall device efficiency. The large difference between dark and illuminated current also reflects a high light-to-electricity conversion potential. Additionally, the improved photocurrent in the heterostructure can be interpreted as an increase in short-circuit current density (J_{sc}), which is a critical parameter for photovoltaic performance. The pronounced nonlinearity and diode-like behavior further suggest that the heterostructure exhibits photovoltaic junction properties, making it suitable for solar harvesting systems.

3.13 Mott–Schottky Analysis

The Mott–Schottky (M–S) analysis provides critical information on the semiconductor type, flat-band potential (V_{fb}), and donor carrier concentration (ND), which are essential parameters in evaluating the PEC behavior of semiconductor-based electrodes (Gelderman *et al.* 2007). In the present study, a comparative M–S analysis was performed for both pristine SnO_2 (Fig. 14) and the multilayer $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructure (Fig. 15), with the respective $1/C^2$ vs voltage plots yielding distinct electrochemical characteristics. As shown in the extracted linear regions, both materials exhibit negative slopes, confirming their intrinsic n-type conductivity, consistent with the known electron-dominated transport behavior of SnO_2 and TiO_2 systems.

The slope of the M–S plot for SnO_2 was measured at $-2.92 \text{ V} \cdot (\text{nF})^{-2}$, whereas a steeper slope of $-3.45 \text{ V} \cdot (\text{nF})^{-2}$ was observed for the $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ system. According to the Mott–Schottky relation. The slope is inversely proportional to the donor concentration. Thus, the steeper slope in the composite film implies a lower carrier density compared to the pure SnO_2 electrode (Pyun and Kim, 1991). Using estimated dielectric constants of $\epsilon \approx 9.0$ for SnO_2 and $\epsilon \approx 15.0$ for the heterostructure, the calculated donor concentrations were approximately $5.37 \times 10^{12} \text{ cm}^{-3}$ for SnO_2 and $2.72 \times 10^{12} \text{ cm}^{-3}$ for the $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ system.

This reduction in ND within the heterostructure may be attributed to the band alignment and interfacial charge redistribution induced by the incorporation of TiO_2 and $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ layers, which modulate the space charge region and limit free carrier availability.

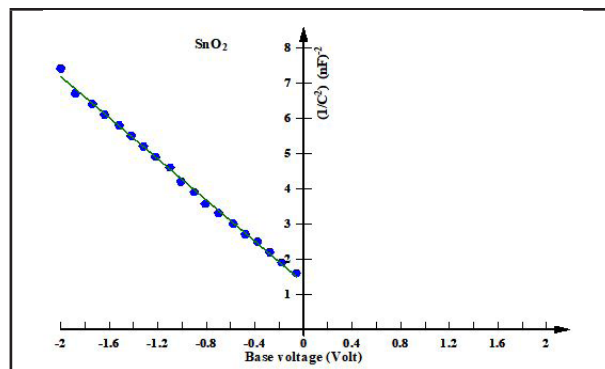


Fig. 14: Mott–Schottky (M–S) plot of SnO_2 thin film, showing a linear region with a negative slope in the $1/C^2$ vs applied potential curve

The flat-band potential (V_{fb}) further reflects the electronic structure at the semiconductor–electrolyte interface. For SnO_2 , the intercept yielded a V_{fb} of approximately -0.45 V vs. reference electrode (equivalent to -0.24 V), consistent with the behavior of accumulation-layer n-type oxides. However, for the composite heterostructure, a substantial positive shift in V_{fb} to $+0.22 \text{ V}$ vs. reference ($+0.43 \text{ V}$) was observed. This shift indicates a lower Fermi level position and enhanced band bending, which favors more efficient separation and extraction of photo-generated charge carriers (Nguyen *et al.* 2020). The reduced intercept value ($0.85 (\text{nF})^{-2}$ vs. $1.32 (\text{nF})^{-2}$ in SnO_2) suggests an interface with fewer trap states and improved surface energetics in the multilayer configuration.

Collectively, these findings demonstrate that the multilayer heterostructure promotes enhanced charge management through its modified electronic structure. The reduction in donor concentration, along with the positive V_{fb} shift, supports the formation of a favorable cascade band alignment, conducive to efficient electron transport and suppressed charge recombination. These properties are of particular importance for applications in photoelectrochemical water splitting and photovoltaic energy conversion, where strong interfacial fields and low recombination rates are essential for optimal performance. A detailed comparison of the extracted Mott–Schottky parameters and their physical implications is presented in Table 6, highlighting the differences in slope, intercept, carrier density, and energetic alignment between the two systems.

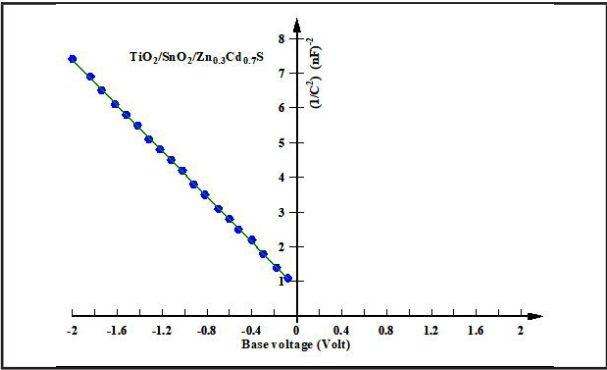


Fig. 15: Mott–Schottky (M–S) plot of $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ system, showing a linear region with a negative slope in the $1/C^2$ vs applied potential curve

Table 6. Mott–Schottky analysis results and interpretations for SnO_2 and $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ films

Parameter	SnO_2	$\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$	Key Interpretation
Slope (m) $[\text{V} \cdot (\text{nF})^{-2}]$	-2.92	-3.45	Higher slope indicates lower donor density in the heterostructure, favoring charge separation.
Intercept (b) $[(\text{nF})^{-2}]$	1.32	0.85	Lower intercept in the heterostructure suggests enhanced interfacial capacitance and charge transport.
Semi conductor Type	n-type	n-type	Both films exhibit electron-dominated conduction, essential for photoanode applications.
Flat-Band Potential (V)	-0.45 V	+0.22 V	Positive shift in V_{fb} implies stronger band bending and better electron extraction in the composite.
Flat-Band Potential (V)	-0.24 V	+0.43 V	Indicates a more favorable band alignment for photocatalytic or PEC applications in the heterostructure.
Dielectric Constant (ϵ)	~9.0	~15.0	Higher ϵ in the heterostructure improves screening, reducing recombination losses.
Donor Concentration (ND) $[\text{cm}^{-3}]$	5.37×10^{12}	2.72×10^{12}	Lower ND in the heterostructure reduces free carrier recombination, aiding photovoltaic performance.

4. CONCLUSION

In this work, a multilayer $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ heterostructure was successfully synthesized and characterized to evaluate its structural, morphological, optical, and electronic properties for optoelectronic applications. The XRD results confirmed the polycrystalline nature and phase purity of each component, while the observed reduction in crystallite size and increase in microstrain in the composite indicated strong interfacial interaction and enhanced structural disorder conducive to charge separation. Further, the formation of a dense and uniform film morphology was confirmed by SEM and AFM analyses.

Optical investigations revealed a systematic reduction in the bandgap energy upon $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ incorporation, accompanied by an increase in the absorption coefficient and refractive index, highlighting the composite’s superior light-harvesting capability in the visible range. Mott–Schottky analysis confirmed the n-type semiconducting behavior of all films, with the heterostructure exhibiting a more positive flat-band potential and reduced donor concentration, indicative of favorable band bending and suppressed carrier recombination.

Moreover, I–V measurements under dark and illuminated conditions demonstrated significantly enhanced photocurrent response and reduced dark current in the $\text{TiO}_2/\text{SnO}_2/\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ system, affirming its improved PEC performance. These enhancements are attributed to the cascade energy band alignment and synergistic effects among the constituent layers, which collectively promote efficient charge separation and transport.

Despite these promising outcomes, certain limitations remain. The study was conducted under controlled laboratory conditions, and real-world environmental effects (such as temperature fluctuations, humidity, and long-term stability) were not examined. Additionally, the precise contribution of each interfacial layer to charge dynamics requires further investigation through advanced time-resolved spectroscopy or impedance analysis.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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