

Research Article

Effect of sulfur-modified zinc oxide thin layers on structural, morphological, optical, and photocatalytic properties for environmental applications

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ABSTRACT

This study investigates the impact of sulfur (S) doping on the structural, surface morphological, and optical properties of zinc oxide (ZnO) thin films, alongside their potential applications in photocatalysis. X-ray diffraction (XRD) analysis confirmed that the films maintained a hexagonal structure without any impurities or additional phases. The incorporation of 2 wt% S into ZnO led to a reduction in crystallite size from 26.71 nm to 24.59 nm. Scanning electron microscopy (SEM) images showed modifications in surface morphology due to the doping process. Energy dispersive X-ray Spectroscopy (EDS) analysis confirmed the presence of S in the films. Atomic force microscopy (AFM) analysis revealed an increase in root mean square (RMS) roughness from 3.321 nm to 3.879 nm following doping. Ultraviolet-visible (UV-VIS) spectroscopy measurements indicated a decrease in the band gap for the 2 % S-doped ZnO sample from 3.26 eV for pristine ZnO to 3.23 eV. The 2 %-doped ZnO sample exhibited enhanced efficacy in degrading methylene blue dye when exposed to UV and sunlight. The trapping test identified $\cdot\text{OH}$ and h^+ as the primary active species in the photocatalytic processes. Additionally, the thin film demonstrated improved stability and reusability after six recycling cycles, suggesting its potential for wastewater treatment. Thus, S-doped ZnO emerges as a promising material for environmental applications.

1. Introduction

The surge in industrial activities has led to a marked increase in waste effluents, severely affecting environmental quality. The textile industry is a significant contributor to this issue, primarily through water pollution, as it generates large volumes of wastewater and consumes substantial amounts of purified water [1,2]. This industry employs various synthetic organic dyes, such as Congo Red (CR), rhodamine B (RhB), Methylene Orange (MO), and Methylene Blue (MB), all of which are hazardous to human health. Therefore, it is crucial to address this toxic waste using treatment methods that are both low-cost and cost-effective and environmentally sustainable. Photocatalysis stands out as a particularly effective and promising approach, offering benefits for both energy and environmental applications [3]. This method benefits from the use of renewable energy sources, such as direct sunlight, and operates under ambient conditions of temperature and pressure [4]. The degradation of pollutants in sunlight involves the generation of highly reactive oxygen species on the photocatalyst

surface [5]. The use of metal oxide semiconductors in photocatalysis is gaining attention due to their potential in various ecological applications, including the removal of organic pollutants from water resources [5,6]. Zinc oxide (ZnO) is a predominant photocatalyst, characterized by its suitable direct band gap (~ 3.2 eV), high exciton binding energy (60 meV), excellent photosensitivity, chemical stability, non-toxicity, biocompatibility, and affordability [7,8]. However, its effectiveness is limited by structural defects that facilitate the rapid recombination of photogenerated electron-hole pairs, thereby reducing its photocatalytic efficacy and application scope [3]. Furthermore, ZnO's dependence on the ultraviolet (UV) portion of the solar spectrum, which constitutes only 4 % of solar energy, is a limitation [9]. Enhancing ZnO's optical absorption to cover a broader spectrum of visible light and reducing the recombination rate of electron-hole pairs can improve its photocatalytic performance. Techniques such as doping, noble metal deposition, heterojunction formation, and morphological manipulation are viable strategies to achieve these enhancements [9–11].

Studies have explored the doping of ZnO with a variety of elements,

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including alkali, transition, noble, or rare earth metals, as well as non-metallic elements, to reduce the ZnO band gap and enhance the generation of electron-hole pairs under visible and solar radiation [12–15]. Recently, the focus has shifted towards non-metal doping of ZnO, which has gained considerable attention. Research has shown that non-metal dopants, such as sulfur (S) [16], nitrogen (N) [17], carbon (C) [18], and fluorine (F) [19] can extend the optical absorption edge of ZnO to longer wavelengths. These dopants also create new localized electron sites within the ZnO band gap, effectively trapping photogenerated electrons [18,19]. This process prolongs the lifetime of charge carriers and reduces electron-hole recombination. Sulfur, in particular, is an effective non-metal dopant for ZnO due to its large atomic radius and strong electronegativity, which allow it to occupy oxygen vacancies and trap electrons [20]. Furthermore, sulfur's group similarity to oxygen suggests it can enhance photocatalyst efficiency [21]. Studies have demonstrated that S-doped ZnO nanostructures exhibit superior photocatalytic performance compared to undoped ZnO. For instance, Rati et al. [22] synthesized S-doped ZnO nanorods using a seed-mediated hydrothermal process for RhB dye removal, achieving a degradation rate of 92 % in 150 min under visible light. Mirzaeifard et al. [20] reported a 100 % degradation rate in 60 min for RhB dye using S-doped ZnO nanoparticles synthesized via the hydrothermal method under visible light. Joy et al. [23] achieved an 81.4 % degradation rate in 180 min for MB dye using S-doped ZnO nanoparticles synthesized by the thermos-evolution method under UV and visible lamps. A major challenge in scaling up photocatalysis technology is the use of photocatalyst in powder form, which complicates separation after the reaction. Additionally, the reusability and stability of the catalyst are compromised due to the contaminant absorption on its surface, leading to reduced efficiency [24]. Thin-film based photocatalysis offers a promising solution to these challenges, with fabrication methods including electrodeposition [25], magnetron sputtering [26], pulsed laser ablation [27], sol-gel [28] and spray pyrolysis [29]. Among these, sol-gel dip coating is particularly advantageous due to its cost-effectiveness, low operating temperature, and suitability for large-area applications [30]. However, there is a scarcity of studies on the photocatalytic properties of S-doped ZnO thin films. This investigation focuses on developing S-doped ZnO thin films for dye removal applications. The study demonstrates the ability to tailor structural, morphological and optical properties, such as band gap energies, of thin films by adjusting the sulfur doping content. The novelty of this study lies in the first-time deposition of S-doped ZnO thin films using the sol-gel dip coating method. S-doped (2 % and 5 %) ZnO thin films were grown on glass substrates using this method. FESEM and AFM were employed to analyze the surface structures of thin films. The catalysts produced showed effectiveness in wastewater treatment when exposed to sunlight.

2. Experimental procedure

2.1. Chemical and materials

The study utilized several chemicals, including zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99 % purity, MERCK], sodium sulfate anhydrous [Na_2SO_4 , ≥ 98 % purity, Sigma-Aldrich], monoethanolamine (MEA) [$\text{C}_2\text{H}_7\text{NO}$, 99 % purity, Sigma-Aldrich], ethanol [$\text{C}_2\text{H}_6\text{O}$, 99.8 % purity, VWR], methylene blue dihydrate (MB) [$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 2\text{H}_2\text{O}$, 99 % purity, Sigma-Aldrich], and glass slides with dimensions of $25.0 \times 37.6 \text{ mm}^2$ and a thickness of 1–1.2 mm were used as substrates for film deposition. Thin films were fabricated at room temperature using a dip-coating device (HOL-MARC HO-TH-02B).

2.2. Synthesis of thin films

The procedural steps for sample preparation using the sol-gel and dip-coating methods are illustrated in Fig. 1. Both undoped and S-doped ZnO thin films were deposited onto glass substrates, thoroughly cleaned using an ultrasonic machine with acetone, methanol, distilled water,

and ethanol for 15 min, followed by drying. Initially, a 0.4 M solution of zinc acetate was prepared in a mixture of ethanol and MEA (30 mL and 0.4 mL respectively). This solution was stirred for thirty minutes at room temperature and then heated to 50 °C for two hours until it became transparent. Deionised water served as the solvent for preparing a sodium sulfate solution of 10 mL for each model at two different weight percentages, based on mass concentration (5 % and 2 %). This solution was stirred for one hour at 80 °C. The resulting solutions were then combined with the previously prepared pure zinc oxide and stirred for two hours at 50 °C. The prepared solutions were kept at room temperature for 48 h before being applied via dip coating. Each layer was dip-coated onto glass substrates, and all thin films were dried for 15 min at 300 °C. The process was completed by annealing in an oven set at 500 °C for two hours after the deposition of twenty layers.

2.3. Characterization tools

The crystal structure was determined using XRD with a D8 ADVANCE X-ray diffractometer equipped with a Cu-K α radiation source ($\lambda = 1.54184 \text{ \AA}$) within the 20–80° range. Surface morphology was examined using a scanning electron microscope (SEM; JSM 7600F JEOL, Japan), and the elemental composition of each film was analysed using the associated energy dispersive X-ray spectroscopy (EDS) unit. An atomic force microscope (AFM; Dimension-3100, Veeco) was employed to assess the surface roughness topography of the material. The optical properties and absorbance spectra of the MB were evaluated using a SPECTROSCAN 80D UV–visible spectrophotometer in the wavelength range of 190–1100 nm.

2.4. Photocatalytic tests

The photocatalytic performance of the synthesized thin films, namely pristine ZnO and S-doped ZnO, was assessed using two different irradiation sources. The experiments were conducted under natural sunlight on a sunny day in October 2024 in Khenchela, Algeria, between 11 am and 3 pm with, an average flux of approximately 480 mW/cm², and under UV light using a Philips G15T8 (15 W, $\lambda = 251 \text{ nm}$) lamp positioned at a distance of 10 cm. An aqueous solution of MB dye was used to evaluate the UV and solar light-driven photocatalytic reactions of the samples. The methodology applied in each experiment, which is effective for thin film samples, involved placing a 2 cm $\times$ 2 cm thin film in 10 ml of a pH $\sim$ 7.5, $2.5 \times 10^{-5} \text{ mol L}^{-1}$ MB solution. To establish an adsorption-desorption equilibrium between the catalysts and the dye components, the catalyst-containing solutions were agitated in the dark for 30 min before illumination. Subsequently, the glass beakers were exposed to direct sunlight and ultraviolet rays. Every half hour, 3 ml of the pollutant was extracted for exposure to sunlight. The concentration

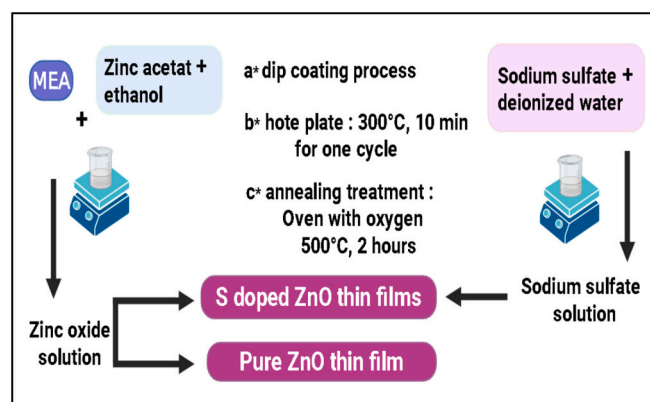


Fig. 1. Illustrates the steps in preparing thin film samples using the dip-coating technique.

of MB in the 500–750 nm wavelength region was measured using a SpectroScan 80D UV–vis spectrophotometer. After promptly measuring absorbance A , the utilized fluid (3 ml) was returned to the original solution to a consistent amount of MB. The procedure for UV illumination at different times was analogous. The photocatalytic degradation efficiency (%) and dye concentration ratios were calculated using eq. (1), based on the Beer-Lambert law applied to the dye's peak absorption wavelength ($\lambda = 664$ nm) [31]:

$$\text{Dye degradation rate } (\eta)\% = \frac{C}{C_i} \times 100 = \frac{C_i - C_t}{C_i} \times 100, (C_i = A_i) \quad (1)$$

Where C_t denotes the concentration at the time of measurement and C_i represents the initial concentration ($t = -30$ min).

3. Results and discussion

3.1. Structural investigation

The X-ray diffraction analysis of S-doped ZnO thin films, along with pure ZnO thin films at different dopant levels, is illustrated in Fig. 2. Within the diffraction angle range of 30° and 70° , seven distinct peaks are identified, corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes. The peaks are consistent with the ZnO reference pattern, as specified by the standard ICDD card number 00–036–1451. The XRD results showed no evidence of secondary phases or impurities, such as peaks related to ZnS or sulfur, likely due to the low S concentration (below 5 %), highlighting the success of the doping method. The graphical data confirms that all samples possess hexagonal wurtzite crystal structures, associated with the space group P63mc [32,33]. Among the various ZnO phases, the hexagonal wurtzite ZnO phase is recognized to be the most thermodynamically stable [34]. The crystalline quality is evaluated through the intensity and full width at half maximum (FWHM), as noted in previous studies. Each sample exhibits a pronounced and sharp peak corresponding to the (002) plane, and no shift in the XRD peaks was observed with the addition of S dopant. This suggests that ZnO crystals preferentially orient perpendicular to the substrate surface along the c-axis [35]. The (002) plane, being the dominant peak, is chosen for further analysis and calculations. Microstructural parameters, such as crystallite size (D), dislocation density (δ), and micro-strain (ϵ), were determined using XRD are presented in Fig. 3(a), and x-ray density, specific surface area, and bond length are presented in Fig. 3 (b). The Debye-Scherrer equation was applied to calculate the crystallite size [34]:

$$D_{(002)} = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where k is the correction constant (0.94), λ is the X-ray wavelength (1.54 Å), β is the FWHM, θ is the Bragg's angle, and $D_{(002)}$ is the crystallite size based on the (002) plane. Eqs. (3) and (4) were used to compute the dislocation density (δ) and micro-strain (ϵ) [36,37].

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

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

The following equations were utilized to determine the lattice parameters ($a = b$ and c), interplanar spacing (d), and volume of the unit cell (V_{cell}) for the hexagonal ZnO structure (as displayed in Table 1) [38,39]:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3a^2} (h^2 + k^2 + hk) + \left(\frac{1}{c}\right)^2}} \quad (5)$$

$$2d_{hkl} \sin \theta = \lambda \quad (6)$$

$$V_{\text{cell}} = \frac{\sqrt{3}}{2} a^2 c \quad (7)$$

The Zn—O bond length (l) for the hexagonal structure of ZnO was calculated using the following relations [40]:

$$l = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \quad (8)$$

In the wurtzite structure, the positional parameter (u) quantifies the displacement of one atom relative to the next atom along the c-axis. The parameter u in the wurtzite structure can be determined using the following formula [40]:

$$u = \frac{a^2}{3c^2} + 0.25 \quad (9)$$

X-ray density ($\rho_{\text{x-ray}}$) and specific surface area (S^*) were derived from the following equations [41,42]:

$$\rho_{\text{x-ray}} = \frac{ZM}{V_{\text{cell}} N_a} \quad (10)$$

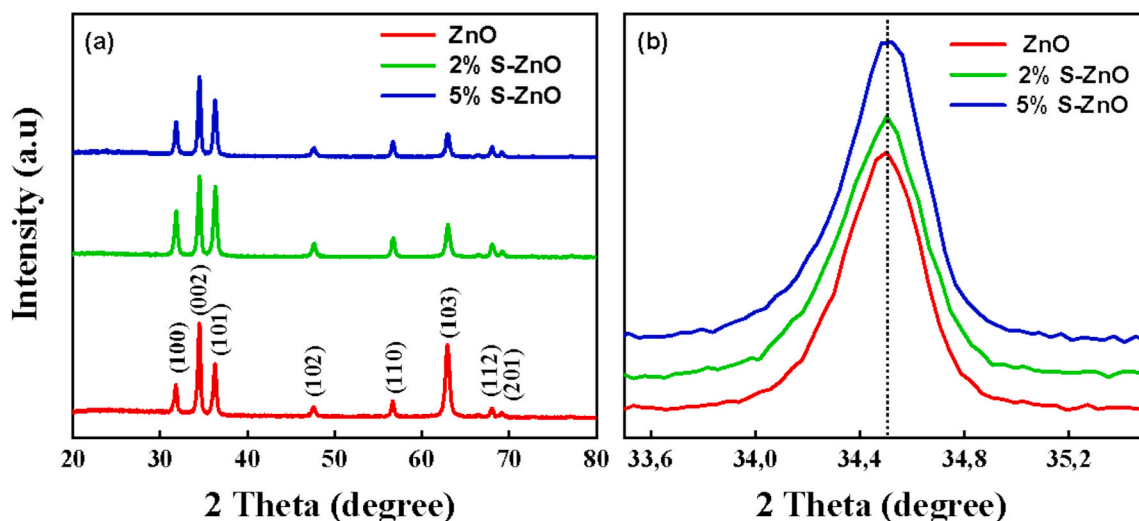


Fig. 2. (a) XRD patterns of undoped and S-doped ZnO nanostructured thin films with different S doping concentrations, and (b) XRD intense diffraction peaks (002) of samples.

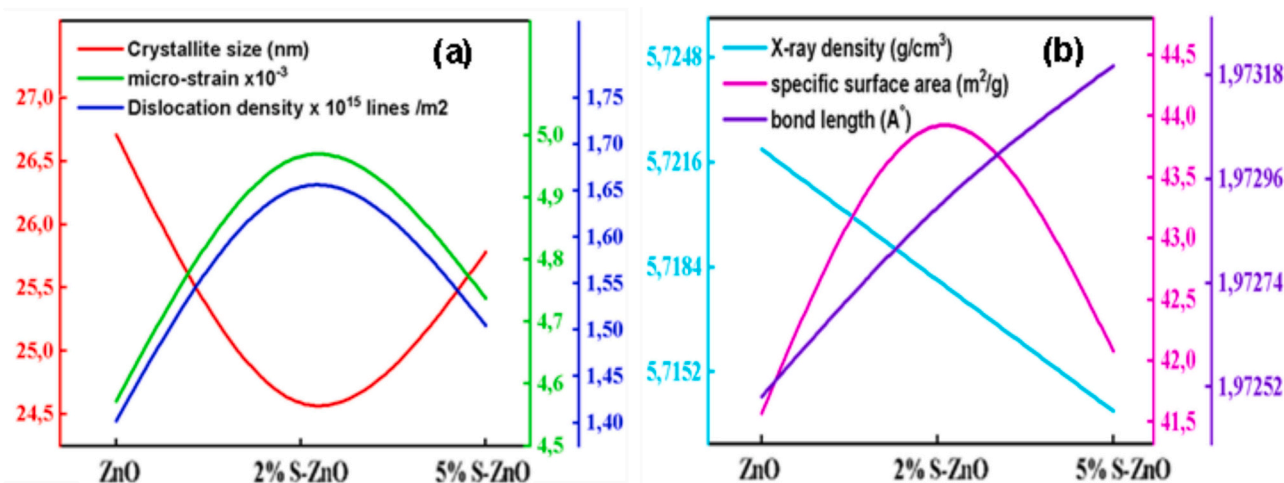


Fig. 3. Structural parameters (a) crystallite size, dislocation density, and micro-strain, and (b) x-ray density, specific surface area, and bond length.

Table 1

Structural parameters derived from XRD data for all thin films deposited using the dip coating technique.

Samples	(hkl)	dhkl (Å ⁻¹)	lattice parameters (Å ^o) a = b < c		Volume V _{celle} (Å ³) ³
ZnO	(100)	2.8093	3.2414	5.1924	47,246
	(002)	2.5974			
2 % S-ZnO	(100)	2.8072	3.2418	5.1939	47,271
	(002)	2.5964			
5 % S-ZnO	(100)	2.8082	3.2421	5.1952	47,292
	(002)	2.5959			

$$S^* = \frac{6000}{\rho_{x\text{-ray}} D} \quad (11)$$

where a, b, and c are the lattice parameters, Z is the coordination number of the unit cell (i.e. the number of atoms per unit cell), M is the molecular weight of the sample, and N_A is Avogadro's number.

The crystallite size for the 2 % S-doped ZnO film decreased from 26.71 nm, as observed in pure ZnO, to 24.59 nm, as depicted in Fig. 3(a). Notably, the crystallite size of the 5 % S-doped ZnO film was slightly larger than that of the 2 % S-doped ZnO film. Research has shown that doping ZnO with S results in modifications to crystallite size, with a reduction noted upon the introduction of sulfur [20,22]. This observation implies that the ZnO lattice was doped with low-valent sulfur, suggesting that dopants hinder crystallite growth. Additionally, the research illustrates that dopants cause lattice distortions and defects, leading to increased internal stresses, as evidenced by the rise in microstrains with doping. The positive microstrain values, as shown in Fig. 3(a), indicate tensile strain ϵ which is associated with the presence of impurities or defects, ion exchanges involving atoms with different ionic radii, and mismatches in the lattice constant [43]. The incorporation of sulfur into the ZnO host crystal lattice is likely responsible for tensile strain observed in this study, as it decreases crystallite size and increases lattice parameters. Our findings align with existing literature, where similar observations have been reported for S-doped ZnO [20,22]. Fig. 3(b) illustrates the determined Zn—O bond length values. Based on the ionic radii of O^{2-} (1.40 Å) and Zn^{2+} (0.74 Å), the expected length of the Zn—O bond is 1.9525 Å; however, the calculated values in all films are slightly greater than 1.9725 Å. It is generally accepted that dopants can be incorporated or substituted based on the size of the doping ions and the electronegativity of the atoms involved [44]. Sulfur (S^{2-}), the dopant, has a larger ionic radius (1.84 Å) than oxygen (O^{2-}), which is 1.40 Å. With a Pauling electronegativity of 2.58, sulfur is less

electronegative than oxygen (3.44). This difference in electronegativity is particularly evident when comparing ZnO and ZnS, with values of (Zn, O) (1.65, 3.44) for ZnO and (Zn, S) (1.65, 2.58) for ZnS. Consequently, Zn^{2+} ions exhibit a stronger attraction to O^{2-} ions than to S^{2-} ions [45,46]. It is important to note that shorter bond lengths typically result from a larger difference in electronegativity between elements [46]. Therefore, the S—Zn bond length is longer than the O—Zn bond length between sulfur and zinc (as shown in Fig. 3(b)). This finding suggests the presence of structural defects, particularly oxygen vacancies [47], when sulfur is doped into the ZnO lattice. The specific surface area (S^*) increased from 41.574 to 43.92 m²/g, while the X-ray density slightly decreased from 5.722 to 5.718 g/cm³ (as depicted in Fig. 3(b)).

3.2. Morphological investigation

SEM was utilized to assess the surface morphologies of both undoped and sulfur-doped ZnO thin films, as illustrated in Figs. 4a-c. Grain size and porosity were evaluated using ImageJ software. The data obtained from ImageJ calculations allowed us to create grain size distribution histograms and determine the average grain size. The results are displayed in Fig. 5(a-d). In ImageJ, film porosity is expressed as a percentage area (% area). The SEM images revealed notable changes in surface morphology in relation to the doping levels. Fig. 4(a) presents the SEM image of undoped ZnO, which shows a uniform, homogeneous, and smooth surface with evenly distributed spherical particles, having an average grain size of 268.304 nm and a porosity of 23.216 % (Fig. 4(a, d)). In contrast, the 2 wt% sulfur-doped thin film (Fig. 4(b, d)) displays wrinkles and small spherical particles, with an average grain size of 174.225 nm and a porosity of 15.162 %; these wrinkles are interconnected. These wrinkles increased the film's surface area beyond initial expectations, potentially enhancing catalytic activity. With an increase in sulfur content to 5 wt%, the wrinkles shrank and their density decreased, resulting in average grain size and porosity of 185.535 nm and 21.606 %, respectively (Fig. 4(c, d)). The observed reduction in the grain size of S-ZnO films, compared to pure ZnO, along with the morphological changes, can be primarily attributed to the integration of S atoms into the ZnO lattice [48]. As elaborated in the X-ray analysis section, the microstress values exhibit an increase and become positive, indicating tensile stress. This is due to the larger ionic radius of sulfur compared to oxygen (S^{2-}/O^{2-} : 1.84 Å / 1.40 Å). Such a positive reading implies the presence of impurities or defects, ion exchanges involving atoms with varying ionic radii, and mismatches in the lattice constant. Generally, doping induces slight distortions in the crystal structure, as evidenced by the minor changes observed in the doped samples [43]. Notably, the grain size values exceed the crystallite size determined

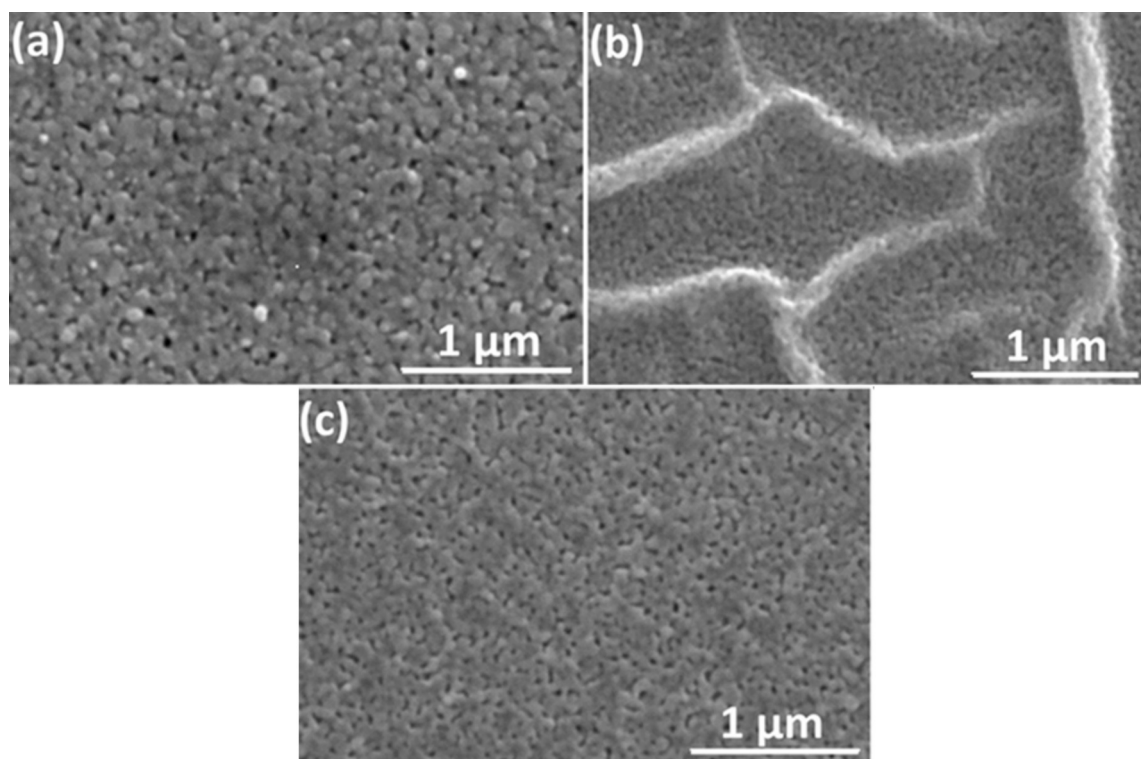


Fig. 4. SEM images of (a) ZnO, (b) 2 % S-ZnO, (c) 5 % S-ZnO thin films.

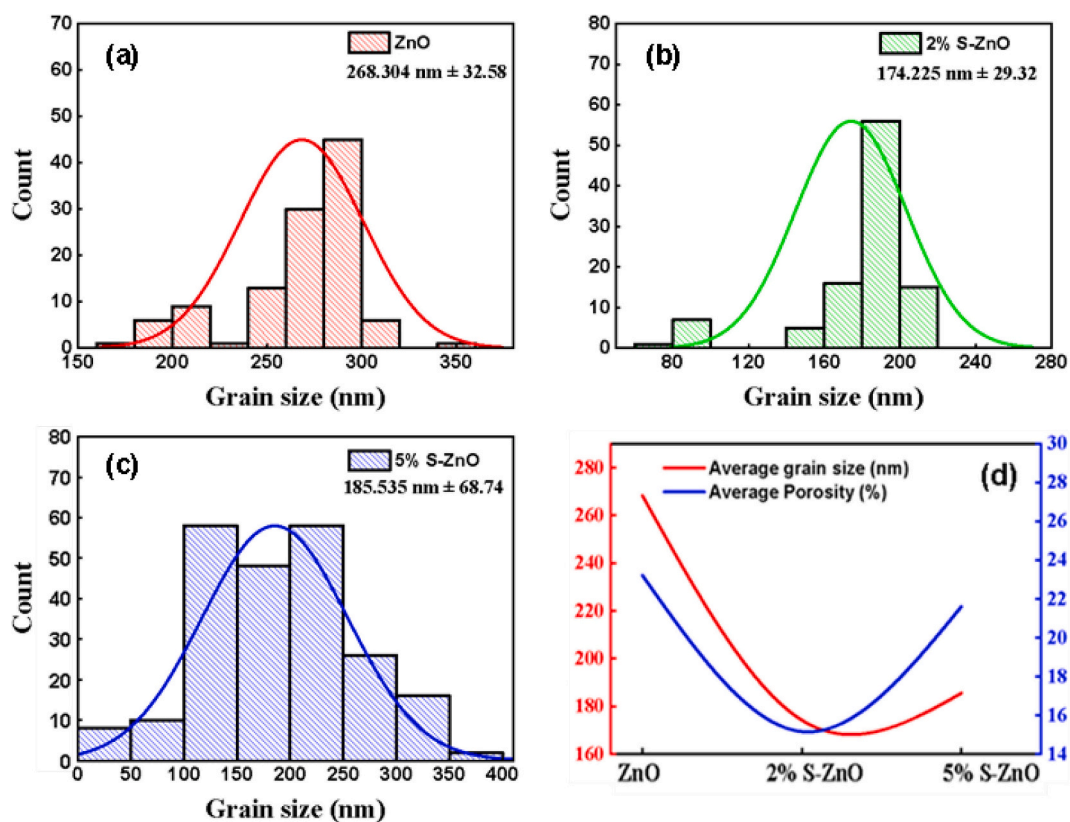


Fig. 5. Grain size distribution histograms for samples (a) ZnO, (b) 2 % S, and (c) 5 % S-ZnO, together with (d) average grain size and porosity.

through SEM and XRD analysis techniques. SEM reveals spherical shapes with small grain sizes, leading to numerous grain boundaries and a resultant scattering effect. In contrast, XRD analysis confirms that the grains are composed of multiple individual crystals. This observation is consistent with the findings of Aradhana and Goktas [49,50], as well as the theoretical work of Straumal [51]. The specific grain boundary area (area-to-volume ratio) can be calculated using the equation $S_{GB} = 1.65/G_S$, where G_S represents the mean grain size [49,50]. The calculated S_{GB} values for pure and sulfur-doped ZnO thin films are approximately 61.5×10^5 , 94.71×10^5 , and $88.93 \times 10^5 \text{ m}^2/\text{m}^3$ for ZnO, 2 % S-ZnO and 5 % S-ZnO thin films, respectively.

Fig. 6(a-c) displays the EDS spectra alongside the composition tables for both undoped and S-doped ZnO samples applied to glass substrates. The analysis confirms the presence of elemental peaks corresponding to Zn, S, and O. It is noteworthy that the atomic percentages of sulfur before activation do not correspond well with the elemental composition observed post-activation, as illustrated in Fig. 3 and elaborated in the XRD section. This inconsistency may be attributed to sulfur's lower Pauling electronegativity (2.58) compared to oxygen (3.44), as well as its larger ionic radius, with ionic radii of $\text{O}^{2-}/\text{S}^{2-}$ being $1.40 \text{ \AA}/1.84 \text{ \AA}$, respectively [45,46,52]. In the pure ZnO thin film, the atomic percentages of oxygen and zinc are 63.81 % and 9.77 %, respectively (Fig. 6(a)). For the 2 % S-ZnO thin film, the atomic percentages of oxygen, zinc, and sulfur are 53.69, 21.98, and 0.46 %, respectively (Fig. 3(b)). Similarly, in the 5 % S-ZnO films, the atomic percentages of oxygen, zinc, and sulfur are 53.08 %, 24.69 %, and 0.99 %, respectively (Fig. 6(c)). As the concentration of the dopant increases, the atomic percentage of oxygen decreases due to the sulfur's integration into the ZnO lattice. Conversely,

the atomic percentage of zinc rises with higher sulfur doping, a necessary adjustment to maintain charge neutrality between the negative charges from sulfur (S^{2-} and O^{2-}) and the positive charges from zinc (Zn^{2+}) within the lattice [53]. Furthermore, the EDS spectrum identifies additional elements such as silicon (Si) and calcium (Ca), likely originating from the glass substrates [54].

3.3. Topographical investigation

AFM serves as a crucial technique for evaluating the quality of surface morphology, as well as for estimating surface area, lateral grain size, and surface roughness. Fig. 7(a-c) displays the two-dimensional (2D) and three-dimensional (3D) AFM images of pristine and S-doped ZnO films. These samples were examined using high-resolution AFM images in contact mode, with a scanning area of $5.0 \times 5.0 \mu\text{m}^2$. The surfaces of the films in Fig. 7(a) and (c) are characterized by regularly formed, homogeneous, dense, and coarse particles. Conversely, Fig. 7(b) reveals an inhomogeneous, irregular film that is less dense than those in Fig. 7(a, c) exhibits wrinkles. Table 2 summarizes the results of Gwyddion's calculations of surface area, mean roughness (S_a), and root-mean-square (RMS) roughness based on these images. The RMS roughness (s_q) values for the pure (a) and S-doped films (b-c) are 3.321, 3.879 and 3.690 nm, respectively. The average roughness values of samples (a), (b), and (c) are 2.646, 3.185 and 2.980 nm, respectively. Consequently, the topography of Fig. 7 (b) is denser than that of Fig. 7(a, c) leading to increased surface area values of (a) 28.66, (b) 29.82, and (c) 29.55 μm^2 . The 2 % S-doped ZnO is marked by inhomogeneity, the smallest grain size, and a densely packed surface, whereas the undoped and 5 % S-doped ZnO films display larger

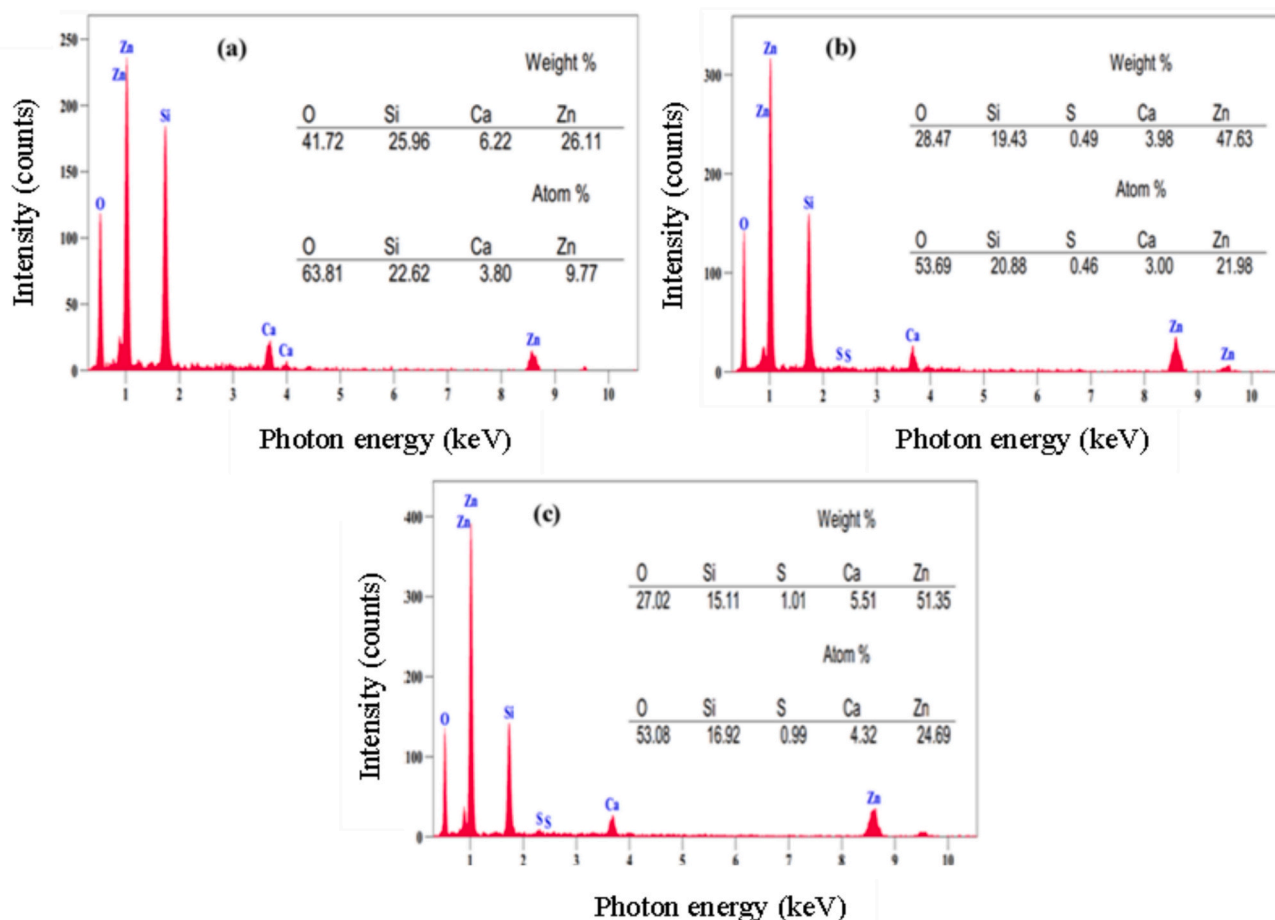


Fig. 6. The EDS images of as-deposited layers (a) ZnO, (b) 2 % S-ZnO, and (c) 5 % S-ZnO.

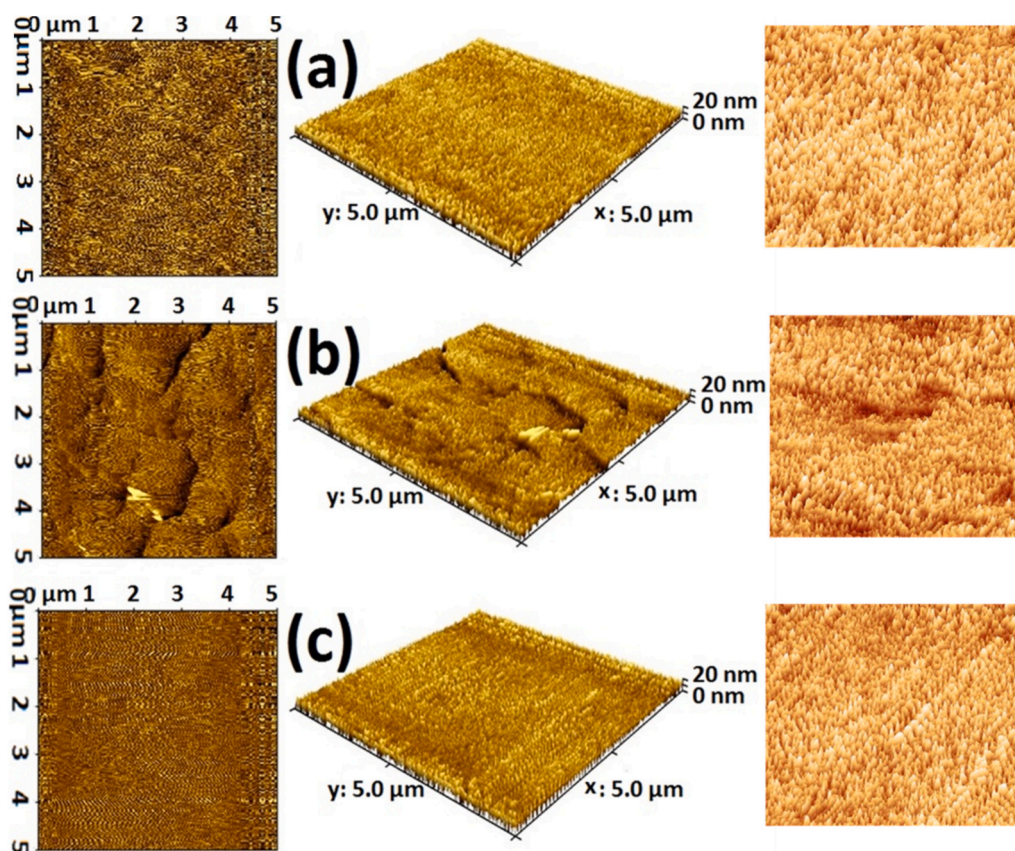


Fig. 7. 2D and 3D AFM images, along with a zoomed-in view of (a) ZnO, (b) 2 % S-ZnO, and (c) 5 % S-ZnO thin films.

Table 2

Root mean square roughness, mean roughness, and surface area of the samples were calculated using Gwyddion software based on AFM images.

Samples	ZnO	2 % S-ZnO	5 % S-ZnO
root mean square roughness (nm)	3.321	3.879	3.690
Mean roughness (nm)	2.646	3.185	2.980
Surface area (μm^2)	28.66	29.82	29.55

grain sizes and less dense surfaces compared to the 2 % S-ZnO. It is apparent that the entire substrate surface is covered with the small grains, with some regions showing agglomerations of grains that are irregularly distributed and rich with wrinkles. A rough surface is advantageous for the adsorption of organic substances and is therefore beneficial for photo electrocatalytic applications [31,55]. These findings align well with our scanning electron microscopy study, which indicated that the RMS roughness increases for the S-ZnO thin film by 2 %.

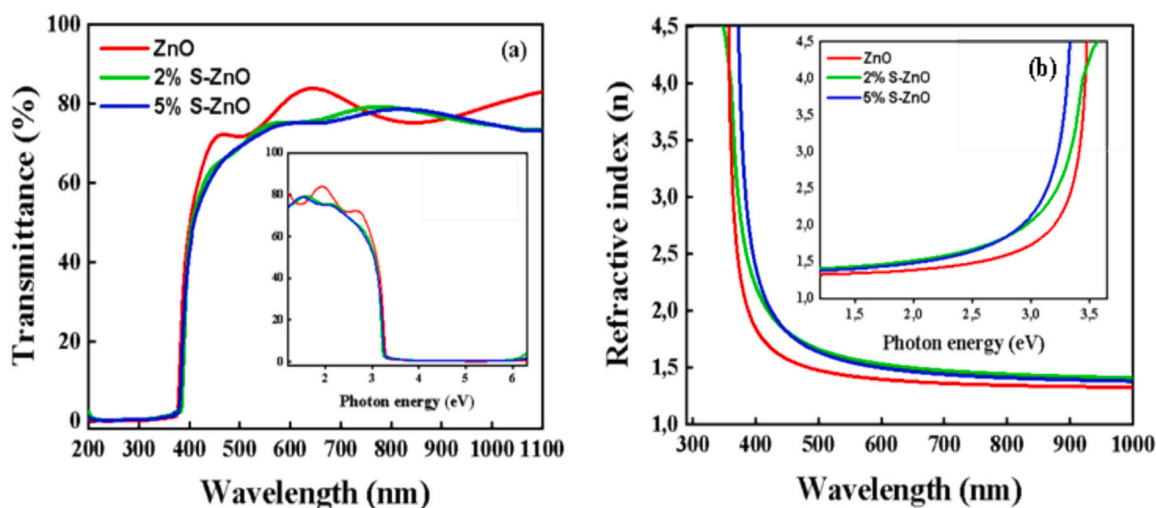


Fig. 8. (a) Transmission and (b) refractive index spectra as a function of the wavelength for all deposited films.

3.4. Optical investigation

To explore the optical characteristics, the transmittance and refractive index spectra of both undoped ZnO and S-doped ZnO thin films were assessed over wavelengths from 190 to 1100 nm, as illustrated in Fig. 8. Within the visible spectrum, the undoped ZnO sample shows a high transmittance, ranging from approximately 75 % to 85 % (Fig. 8(a)). It is apparent that the transmittance of S-doped ZnO thin films diminishes with the incorporation of S. This decline in transmittance can be due to i) the induction of lattice distortion, ii) the emergence of defects, and iii) the increase in scattering centers caused by the addition of S to ZnO thin films. Moreover, the presence of interference fringes in the undoped ZnO thin film signifies the excellent surface quality and optical homogeneity of the final product. Fig. 8(b) displays the refractive index (n) spectra of zinc oxide thin films that include both zinc oxide and sulfur. The values of n and k were computed using Eqs. [31]:

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (12)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (13)$$

$$\alpha = \frac{1}{e} \ln \left(\frac{(1-R)^2}{T} \right) \quad (14)$$

The sample thickness is represented by e , the extinction coefficient by k , the absorption coefficient by α , the reflectivity by R , and the wavelength by λ . The S-introduced samples exhibited higher refractive index values than ZnO thin films in the visible range. The increase in the

n value may be linked to the band gap shift and charge carrier concentration in the ZnO thin film. As observed, S doping reduces the optical band gap of ZnO. Additionally, when used as a dopant, S may modify the concentration of free charge carriers, thereby enhancing the refractive index of ZnO. Higher refractive index values in the lower wavelength or higher energy range result from the alignment of light photon frequencies with the plasma frequency [56]. This alignment leads to resonance between the incident photon and electronic polarization [57], enabling electrons to interact with an oscillating electric field [58,59].

The optical band gap of the studied films was calculated using the Tauc equation, as shown in the following Eq. [31]:

$$(ah\nu) = A(h\nu - E_g)^n \quad (15)$$

In the relationship described, α represents the absorption constant, $h\nu$ denotes photon energy, A is a constant, and E_g signifies the optical band gap value. The exponent n is determined by the nature of the material's transition. In this study, the value of n , which is $\frac{1}{2}$, indicates a direct allowed transition, characteristic of ZnO as a semiconductor with a direct wide band gap [60]. Fig. 9 illustrates the variation in E_g values for each sample. As shown, the E_g value for undoped ZnO thin films is 3.27 eV, while for samples with 2 % and 5 % S doping, the E_g values decrease to 3.23 eV and 3.25 eV, respectively. This reduction in the band gap may result from changes in crystal structures, atomic distances, grain sizes, and the morphology of deposited coatings [15]. Rini and Rati, using a seed-mediated hydrothermal method, prepared S-ZnO nanorods and observed a similar trend in band gap energy with increased sulfur doping [61]. Dutta et al. [62] have reported that the decrease in E_g is due to increased tensile stress as impurities are introduced. The narrow band gap of the coating makes it a promising

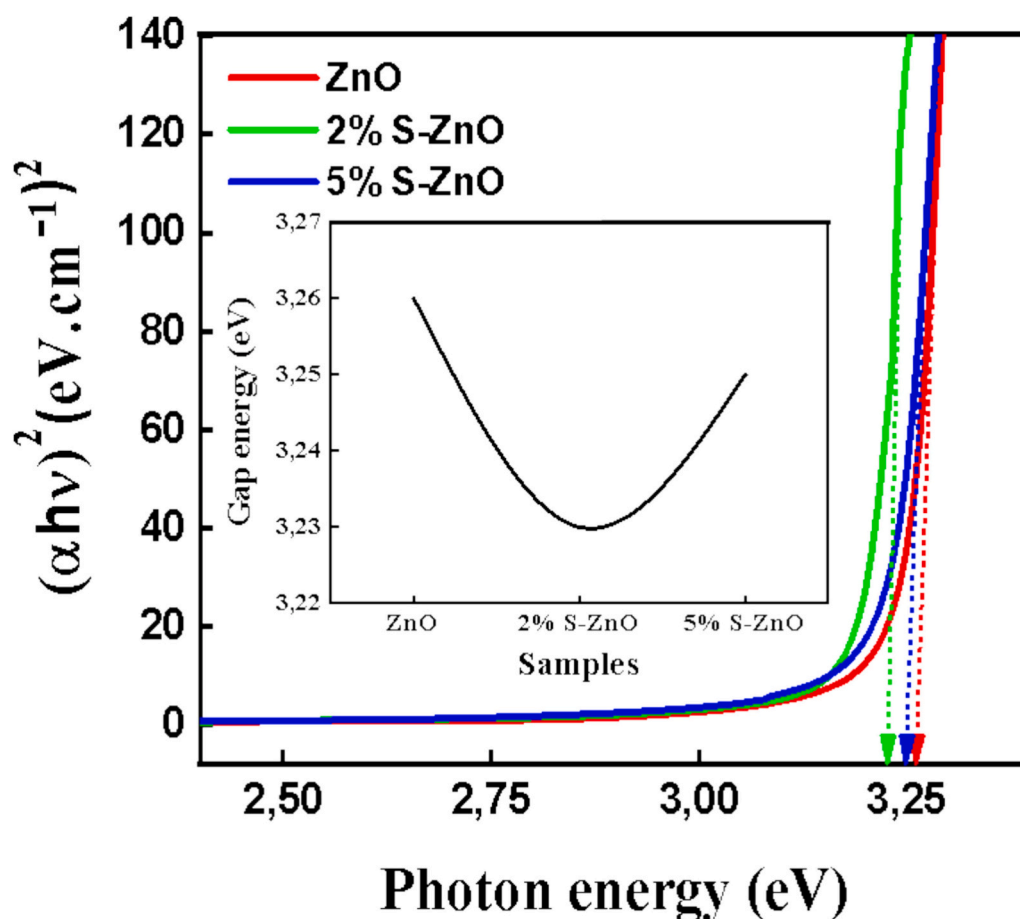


Fig. 9. Energy gap values of the prepared samples.

candidate for photocatalytic applications [63]. However, further experimental studies are necessary to confirm its full suitability.

3.5. Photocatalytic investigation

3.5.1. Photodegradation of MB

After examining the structural, optical, and morphological properties of both undoped and doped ZnO films, we now focus on their photocatalytic activities under UV and natural sunlight illumination. Fig. 10(a-f) displays the optical absorption spectra of the MB solution in the presence of photocatalysts under each light source. The primary absorption peak was identified at $\lambda_{\text{max}} = 664 \text{ nm}$, which is characteristic of MB molecules.

- Under UV light: The spectra were recorded at 15-min intervals. Fig. 10(a-c) illustrates the decline in intensity of the absorption peaks over time, as well as under dark conditions, in the presence of thin films.

Fig. 11(a) presents the results of MB photodegradation efficiency measurements as a function of UV irradiation duration, revealing that S-doped ZnO thin films demonstrated superior MB degradation efficiency compared to pristine ZnO. Notably, the 2 % S-doped ZnO thin film exhibited optimal performance after 50 min. Table 3 provides the effectiveness values obtained, indicating that dye degradation with the various photocatalysts is nearly complete after 50 min of UV light exposure. ZnO doped with 2 % S achieved the highest degradation efficiency among the photocatalysts, reaching 94.69 % at 50 min.

- Under sunlight: the spectra were recorded at 30-min intervals. Fig. 10(d-f) shows the reduction in intensity of the absorption peaks over time, as well as under dark conditions, in the

presence of thin films. The initial blue colour of the solution gradually fades until it becomes colorless as the reaction progresses, indicating the breakdown of the chromophoric structure of MB upon exposure to sunlight. The results of MB photodegradation effectiveness measurements as a function of sunlight exposure time are presented in Fig. 11(b) for further analysis, demonstrating that S-doped ZnO thin films exhibited a higher MB degradation rate than pristine ZnO. Table 3 provides the effectiveness values obtained, indicating that dye degradation with the various photocatalysts is nearly complete after 90 min of direct solar light exposure. ZnO doped with 2 % S demonstrated a greater degree of degradation, achieving 96.71 %, compared to 5 % S-ZnO (89.58 %) and pristine ZnO (76.32 %) at 90 min. Additionally, it is noteworthy that the incorporation of a lower content of sulfur ions into the ZnO matrix significantly enhanced the degradation efficiency of methylene blue.

To the best of our knowledge, the most favourable results for MB degradation under UV and sunlight exposure were achieved using S-doped ZnO-based thin films deposited via the sol-gel dip-coating method. Based on the data described above, we can infer that the following factors contribute to the unique photocatalytic efficiency of S-doped ZnO:

- XRD analysis suggests that a reduction in crystallite size may increase the specific surface area of the film, which is beneficial for enhancing the catalytic activity, as previously documented [64].
- SEM and AFM analyses indicate that larger surface areas contribute to higher photocatalytic activity [65]. Additionally, the increased light absorption of the specimen is primarily due to its rough surface, which features an array of wrinkles that enhance light scattering,

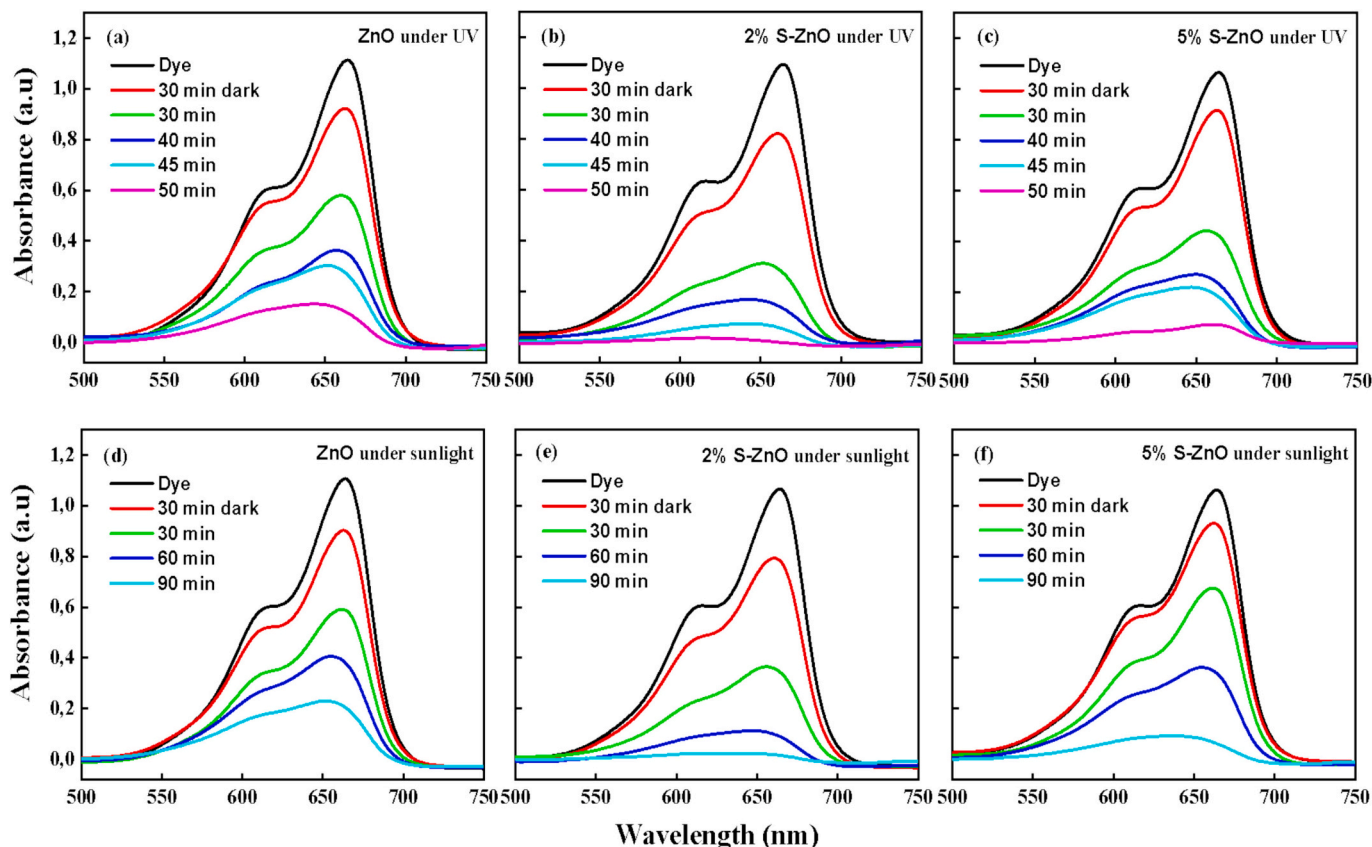


Fig. 10. MB absorbance at different time intervals in the presence of ZnO, and S-doped ZnO catalysts under UV and sunlight irradiation.

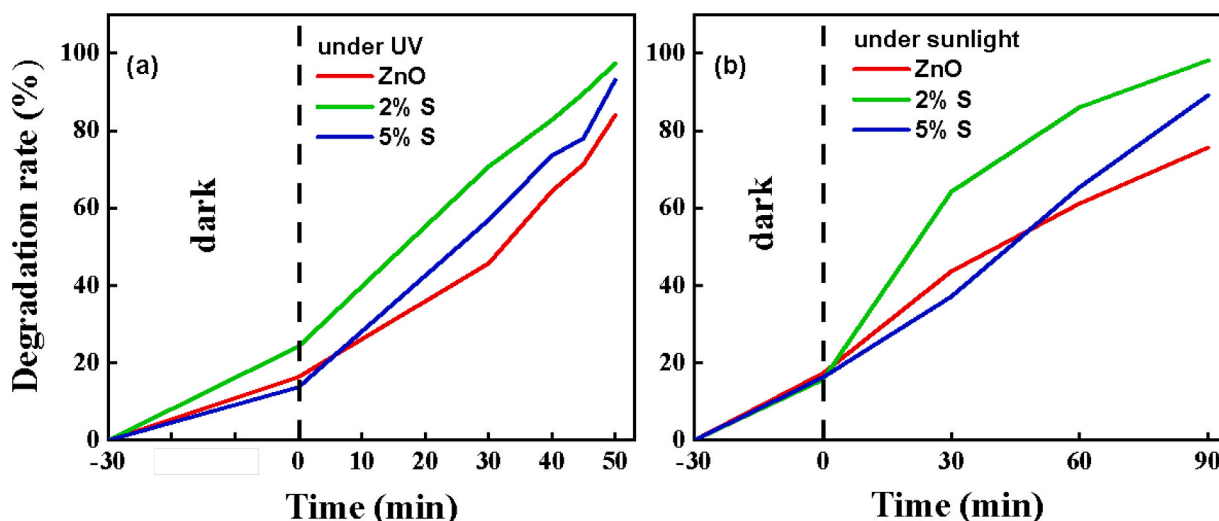


Fig. 11. Degradation rate of MB as a function of time for pristine and S-doped ZnO under (a) UV and (b) sunlight exposure.

Table 3
Kinetic parameters for each catalyst, both and sulfur-doped ZnO.

Samples	Under UV light		Under sunlight	
	k (min ⁻¹)	D (%)	k (min ⁻¹)	D (%)
Pristine ZnO	0.0253	83.99	0.0136	76.32
2 %S-ZnO	0.0476	94.69	0.0237	96.71
5 %S-ZnO	0.0313	93.05	0.0220	89.58

thereby making the photocatalytic procedure more effective under UV and solar irradiation [66].

- From an optical perspective, the reduced band gap energy from 3.26 eV to 3.23 eV allows a greater number of less energetic photons to excite valence electrons, while defect states formed by dopants inhibit electron and hole recombination, thus accelerating the degradation process [67].
- The ability of sulfur doping ions to trap electrons and/or holes on the surface, thereby preventing the recombination process of the (e⁻/h⁺) pair, is another factor contributing to enhanced photocatalytic efficiency [16].

Table 4
Recent published papers on metal and non-metal doped ZnO nanomaterials for photocatalytic degradation of organic pollutants.

Type of dopant	Element in %	Synthesis process	Pollutant/ Light source	Exposure time (min)	Dye degradation %	Ref.
1. Alkaline earth metals	Mg (2.5 wt%)	Sol-gel spin coating (thin film)	MB/ UV	150	72.15	[73]
	Mg	<i>Lupinus albus</i> Leaf Extract (NPs)	MB/ Sunlight	120	99.6	[74]
	Ba (5 wt%)	SILAR (thin film)	MB/ Sunlight	300	95.78	[75]
	Sr (5 wt%)	SILAR (thin film)	MB/ Sunlight	240	94.82	[76]
2. Transition metals	Cu (1 wt%)	ALD (thin film)	MB/ Sunlight	420	90	[77]
	Mn (5 wt%)	Sol-gel dip coating (thin film)	MB/ visible	120	33	[78]
	Cd (5 wt%)	SILAR (thin film)	MB/ UV	150	82.5	[79]
	V (10 wt%)	Spray pyrolysis (thin film)	MB/UV	150	68	[80]
	Ag (5 wt%)	SILAR (thin film)	MB/ UV	180	75	[37]
3. Noble metals	Ag (6 wt%)	Pulsed fs-LA (NPs)	MB/ visible	90	99.5	[81]
	Au (3 wt%)	Wet chemical (NPs)	RhB/ UV	10	100	[82]
	Pd (3 wt%)	Wet chemical (NPs)	MB/ Sunlight	150	48.5	[83]
	La (5 wt%)	Spray- pyrolysis (thin film)	MB/ UV	180	95	[84]
4. Rare Earth metals	Sm (5 wt%)	Sol-gel (NPs)	MB/ Sunlight	60	7.83	
	Nd (0.1 wt%)	Electrospinning- calcination (NPs)	MB/ Halogen lamp	120	100	[85]
	Gd (0.1 wt%)	Calcination (NPs)	AR18/ UV	40	98.28	[86]
	C	Thermo-evolution (NPs)	MB/ UV-visible	150	67.2	[23]
	N	Thermo-evolution (NPs)	MB/ UV-visible	150	78.5	[23]
5. Non-metals	S	Thermo-evolution (NPs)	MB/ UV-visible	150	81.4	[23]
	S (5 wt%)	Hydrothermal (thin film)	RhB/ Visible	150	92	[22]
	S (2 wt%)	Sol-gel dip coating (thin film)	MB/ UV	50	94.69	This study
	S (2 wt%)	Sol-gel dip coating (thin film)	MB/ Sunlight	90	96.71	This study

Table 4 presents the latest research on metal and non-metal doped ZnO nanomaterials used for the photocatalytic degradation of organic pollutants.

3.5.2. Photodegradation kinetic study

The kinetics of MB degradation under light exposure were analysed using the Langmuir-Hinshelwood kinetic model, with samples serving as catalysts. The rate constant (k) for MB degradation is derived from the slope of the first-order kinetic Eq. [68]:

$$k_t = \frac{1}{t} \ln \left(\frac{C_0}{C} \right) \quad (16)$$

where C is the dye concentration at time (t) and C₀ is its initial concentration (t = 0). Table 3 summarizes the experimental data fitted with various catalysts, and Fig. 12(a, b) illustrates the results obtained from this equation. The findings confirm MB photodegradation follows first-order kinetics, with S-doped ZnO films showing enhanced photocatalytic activity compared to undoped ZnO. Specifically, the 2 % S-doped ZnO thin film demonstrated the highest photocatalytic efficiency, with rate constants of 0.0476 min⁻¹ and 0.0237 min⁻¹ under UV and

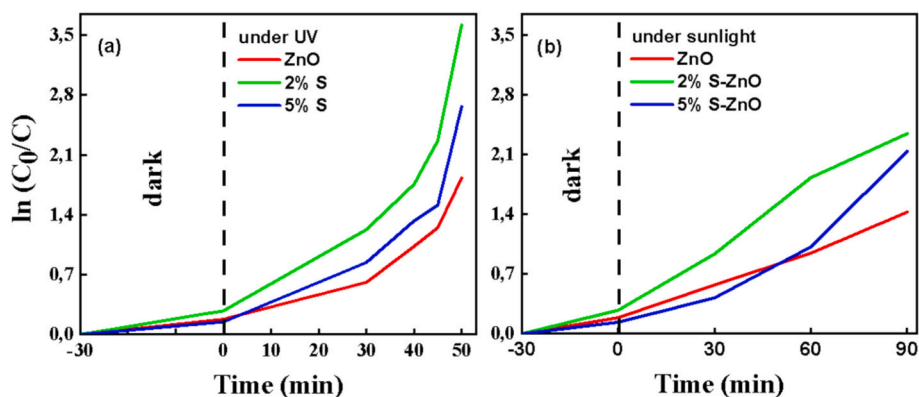


Fig. 12. The reaction kinetics of MB dye degradation for pristine ZnO and S- doped ZnO thin films under (a) UV, and (b) sunlight illumination.

sunlight, respectively, nearly double those of undoped ZnO (0.0253 min^{-1} for UV and 0.0136 min^{-1} for sunlight).

3.5.3. Mechanism of photodegradation behavior

The band edge potentials of the valence band (VB) and conduction band (CB) for ZnO and S-doped ZnO can be determined using a straightforward approach. The Butler and Ginley equations are employed to calculate the E_{VB} and E_{CB} of a semiconductor at its zero-charge state [69,70]:

$$E_{CB} = \chi - E_e - 0.5 E_g \quad (17)$$

$$E_{VB} = E_{CB} + E_g \quad (18)$$

where χ is the absolute electronegativity of ZnO (5.9 eV) and E_e is the energy of free electrons on the hydrogen scale (approximately 4.5 eV). The band gap energies E_g of ZnO, 2 % S-doped ZnO, and 5 % S-doped ZnO films are 3.26 eV, 3.23 eV, and 3.25 eV, respectively. The E_{VB} and E_{CB} values for the 2 % S-doped ZnO thin film are 3.01 eV and -0.21 eV, respectively, while those for perstine ZnO are 3.03 eV and -0.23 eV. The 5 % S-doped ZnO thin film has E_{VB} and E_{CB} values of 3.02 eV and -0.23 eV, respectively. The 2 % S-doped ZnO exhibits a higher conduction band potential than pure ZnO, facilitating the rapid combination of O_2 molecules with excited electrons to form $\cdot O_2^-$ radicals. Consequently, the S dopant effectively traps excited electron, reducing charge carrier recombination.

The photodegradation mechanism of the S-doped ZnO thin film is

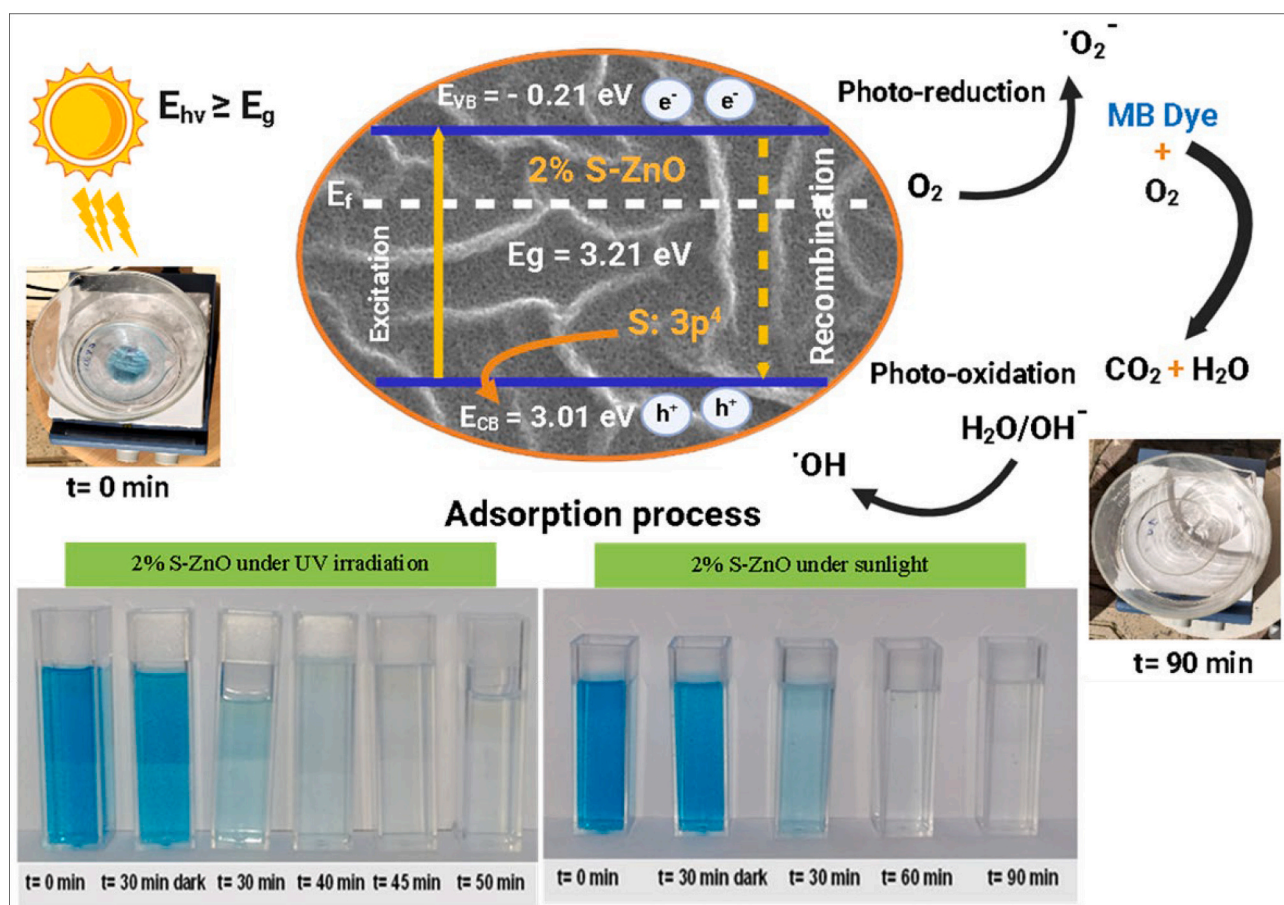
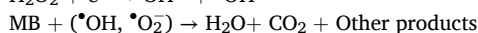
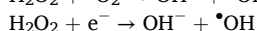
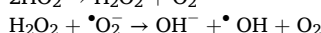
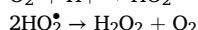
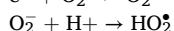
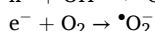
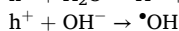
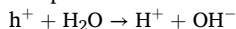
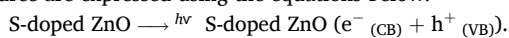


Fig. 13. Photocatalytic dye degradation mechanism of S-ZnO film.

depicted in Fig. 13. In the pristine ZnO, the valence and conduction bands are separated by the Fermi level. The incorporation of sulfur impurities leads to the formation of a new band below the Fermi level, attributed to the generation of free electrons. This impurity effect causes a shift in the Fermi level, thereby modifying the band gap. When a photon with adequate energy strikes the photocatalytic material, a photoexcited electron (e^-) transitions from the VB to the CB, leaving a hole (h^+) in the VB, which facilitates the redox process. Hydroxyl radicals ($\bullet\text{OH}$) are produced when this hole interacts with H_2O molecules. In the S-doped ZnO photocatalyst, the impurity level is positioned below the CB, which may enhance the separation rate of photogenerated charge carriers (e^-/h^+) by trapping the excited electron. The trapped electron can then react with an oxygen (O_2) molecule to form superoxide anions ($\bullet\text{O}_2^-$) radicals. These radicals play a crucial role in the degradation of MB dyes, resulting in the formation of CO_2 , H_2O , and other essential minerals [63]. The degradation reactions of dye under a light source are expressed using the equations below:



3.5.4. Trapping test

Various scavengers, such as ethylenediamine tetraacetic acid disodium salt (EDTA), L-ascorbic acid (AscA), isopropyl alcohol (IPA), and cupric nitrate (CN), were employed in the trapping experiments of the main reactive species. These scavengers were used to trap holes (h^+), superoxide ($\bullet\text{O}_2^-$), hydroxyl radicals ($\bullet\text{OH}$), and electrons (e^-), respectively. A 10 mL solution of MB was separately mixed with 10^{-3} M of each of the four scavengers mentioned. To identify the primary active species in the photocatalytic process, the photocatalytic efficiency was assessed under comparable conditions using experiments conducted without scavengers. The photodegradation efficiency of MB solutions over 2% S-doped ZnO under UV and solar radiation is depicted in Fig. 14(a, b), both with and without various scavengers. As demonstrated in Fig. 14(a), $\bullet\text{OH}$ and h^+ are the principal active species for the degradation of the MB dye under UV light, where the addition of IPA and EDTA significantly reduces the photocatalytic degradation efficiency of 2% S-doped ZnO. Conversely, $\bullet\text{O}_2^-$ plays a dominant role in the degradation of MB

dye when exposed to sunlight (Fig. 14(b)). In contrast, based on the results discussed, e^- plays a minor role in the degradation of MB.

3.5.5. Reusability test

In photodegradation research, the stability and reusability of catalysts are pivotal, as they contribute to the cost-effectiveness of the process by allowing for catalyst recycling. This investigation focused on the reusability of 2 % S-doped ZnO, identified as the most efficient catalyst for degrading MB. Post initial use, the catalyst underwent a cleaning process with distilled water and was dried before reuse. This protocol was consistently applied after each cycle. The degradation process was reassessed in a fresh MB solution with a concentration of 2.5×10^{-5} M. The experiment was conducted six times using 2 % S-doped ZnO catalyst under both UV and sunlight exposure. The results, depicted in Fig. 15(a-c) and Table 5, yield several significant insights.

- A notable increase in degradation percentages was observed between the second and third cycles compared to the first cycle under UV light exposure. This is likely due to the fact that, during the initial measurement, MB adsorption had not yet reached equilibrium and continued during irradiation.
- As illustrated in Fig. 15(a), the degradation percentages of MB dye after four consecutive cycles under UV exposure showed a marked increase within a short irradiation time. This can be attributed to the increased generation of electron-hole pairs with higher light intensity, enhancing photocatalytic activity and dye degradation efficiency. However, a notable decrease was observed in the fifth and sixth cycles.
- The degradation efficiency of MB dye after six consecutive cycles under sunlight exposure showed a slight decrease from 96.71 % to 96.04 % (Fig. 15(b)), indicating the effective recycling performance of 2 % S-doped ZnO under sunlight.
- XRD patterns of the 2 % S-doped ZnO film before and after the sixth cycle under both UV and direct sunlight exposure, as shown in Fig. 15(c), revealed no significant differences except for a reduction in peak intensity. This suggests a loss of crystallinity and a decrease in film thickness, likely due to photo-corrosion, where ZnO at the interface decomposes into Zn^{2+} and O^{2-} ions. These ions dissolve in the solution after leaving the film, resulting in decreased layer thickness and reduced photoactivity degradation [71,72].

In conclusion, these findings underscore the catalyst's robust reactivity, excellent stability, and repeatability, highlighting its substantial

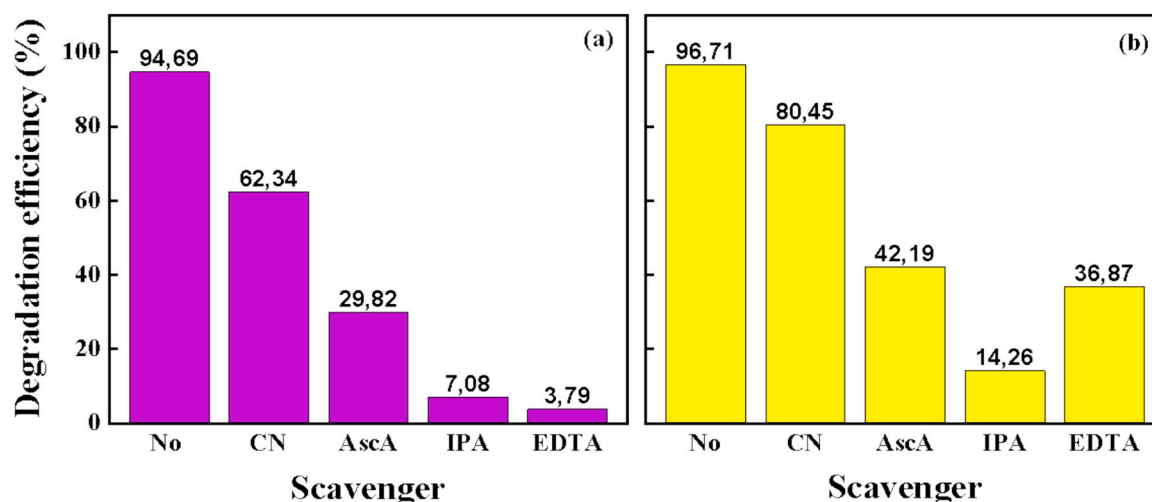


Fig. 14. Degradation efficiency of MB over the 2 %S-ZnO catalyst in the absence and presence of different scavengers under (a) UV irradiation, and (b) sunlight irradiation.

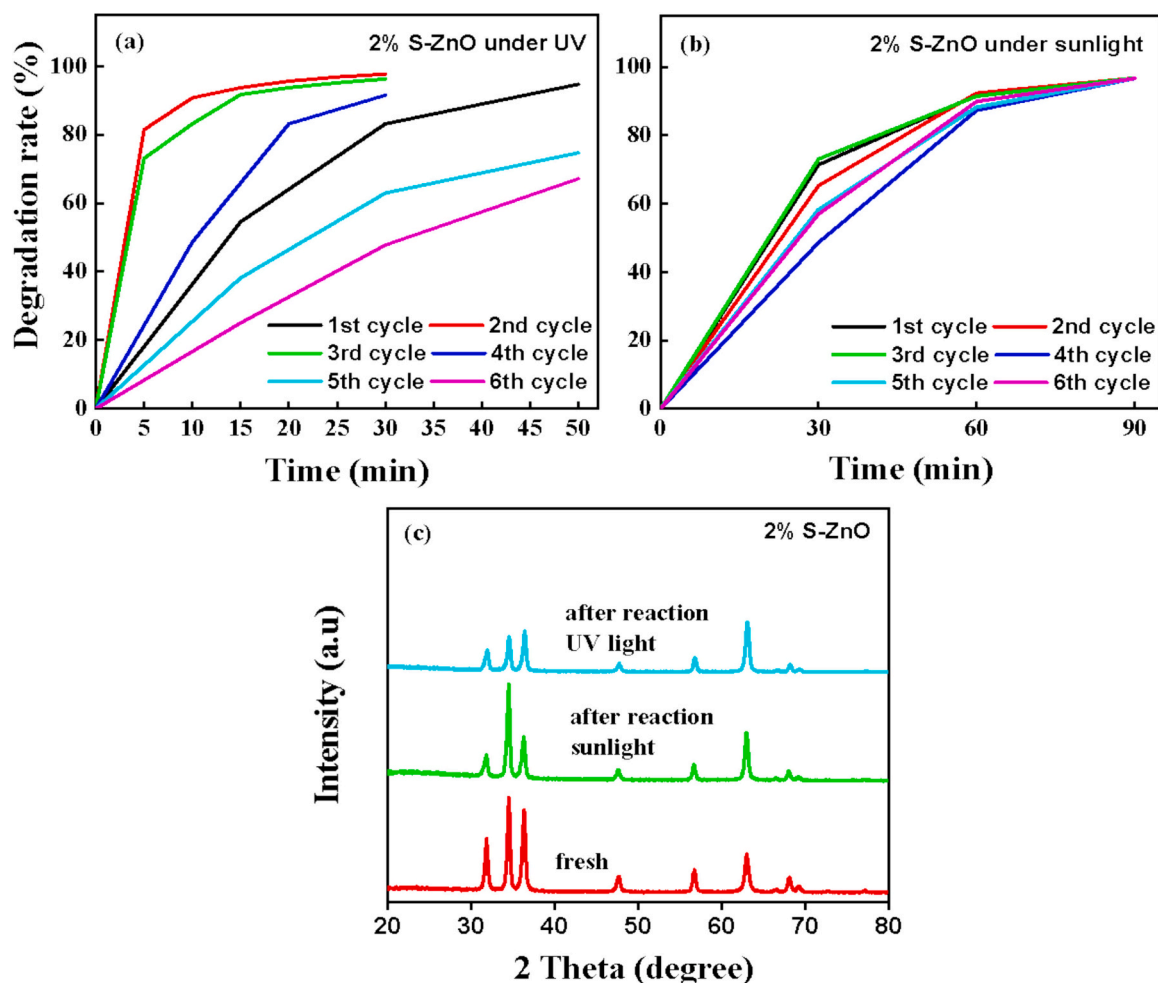


Fig. 15. Photocatalytic test of reusability of the 2 % S-ZnO thin film for MB dye under (a) UV irradiation, (b) sunlight irradiation, and (c) XRD pattern after the sixth cycle of photocatalytic experiments.

Table 5

Reusability of the catalyst, reaction time, and degradation efficiency (D) of methylene blue for 2 %S-doped ZnO.

No. of cycles	Under UV light		Under sunlight	
	D (%)	Time (min)	D (%)	Time (min)
1	94.69	50	96.71	90
2	97.64	30	96.79	90
3	96.21	30	96.50	90
4	89.98	30	96.63	90
5	74.52	50	96.25	90
6	58.46	50	96.04	90

potential for environmental purification, particularly under sunlight irradiation.

4. Conclusion

In this study, pristine and S-doped ZnO thin films were deposited onto glass substrates using the dip-coating technique. The synthesized materials were characterized using various methods, including XRD, EDS, SEM, AFM, and UV-VIS. The deposited thin films were employed as photocatalysts for the degradation of methylene blue under both UV and solar radiation. Compared to pristine ZnO, S-doped ZnO films exhibited superior photocatalytic activity. Under UV and sunlight exposure, the 2 % S-doped ZnO sample achieved the highest photocatalytic performance, with efficiencies of 94.69 % after 50 min and 96.71 % after 90

min, respectively. The active species trapping experiments confirmed that h^+ and $\bullet OH$ play crucial roles in the photocatalytic degradation of MB. Moreover, reusability tests validated the stability and reliability of the film after six consecutive cycles. Further investigation is warranted for this thin film, as it holds a potential as an eco-friendly photocatalyst for a broader range of pollutants; therefore, we suggest that sulfur doping is an effective method to enhance the photocatalytic capabilities of ZnO thin films for environmental applications.

CRedit authorship contribution statement

Khemissi Lahouel: Writing – review & editing, Writing – original draft, Software, Resources, Investigation, Formal analysis. **Abdecharif Boumaza:** Visualization, Validation, Supervision, Methodology. **Abdelkader Djelloul:** Visualization, Validation, Investigation, Conceptualization. **Meriem Gasmi:** Resources, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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