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Effect of Two Different Thicknesses of ZnO Thin Films on the Photocatalytic Activities

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Abstract: ***Zinc oxide (ZnO) thin films with two different thicknesses (600 nm and 800 nm) were successfully deposited on to the glass substrates using a simple and inexpensive SILAR technique. The structural, optical and morphological properties of these films were characterized using X- ray diffraction, UV- vis spectrophotometer, PL spectroflurometer and scanning electron microscope, respectively. The X- ray diffraction analysis shows that the prepared film has polycrystalline nature and the crystallite grown predominantly along (002) plane of hexagonal wrutzite structure. The average transmittance of the films is found to be in the range of 55 - 75 % in the visible region. The optical transmittance and band gap are found to decrease for the film with 800 nm thicknesses. The scanning electron micrographs show that the grain size tends to decrease with increase of film thickness (800 nm). The decrease in PL emission of film of 800 nm could be the result of decreased rate of recombination of electron - hole. The photocatalytic activities of prepared films were investigated for the photodegradation of methylene blue under UV radiation and the photocatalytic efficiency is found to maximum (87.5 % for 80 min) for the film with 800 nm thicknesses.***

Keywords: ZnO thin film, thickness, morphology, photocatalytic activity

1. Introduction

The eradication of dye and toxic organic compounds from paper printing, textile dyeing, color photography, pharmaceutical, cosmetic, and other industries effluents has been studied extensively. Wide band gap, nanosize semiconductors such as TiO_2 and ZnO have been widely examined and utilized as photocatalysts to decompose various organic effluents under UV irradiation because of its abundant availability, chemical stability, cost - effectiveness and its non - toxicity. The current publications show that ZnO can be used as potential semiconductor photocatalyst when compared with TiO_2 [1 - 3]. Many works report the preparation and high photocatalytic efficiencies of ZnO nanoparticles and nanopowders [4, 5]. However, the separation of these catalysts after decomposition process becomes one of the difficult tasks, to avoid this problem ZnO thin films used as catalyst. There are different types physical and chemical techniques used to prepare ZnO thin films such as sputtering [6], pulsed laser deposition (PLD) [7], molecular beam epitaxy (MBE) [8], spraypyrolysis [9], successive ionic layer adsorption and reaction (SILAR) [10 - 12], sol - gel [13], chemical vapour deposition [14]. Among all the methods, SILAR is a simple and inexpensive and has many advantages over the other methods such as low temperature process, large area coatings, easy control of film thickness.

In this study, ZnO thin films were deposited with two different thickness using SILAR technique and the effect of film thickness on the photocatalytic activity against methylene blue dye was studied. The deposited films were characterized for their structural, optical and morphological properties. These studies showed that the increase in film thickness changes morphology, grain size and optical properties of the catalyst resulting enhanced photocatalytic activity.

2. Experimental Details

2.1 Deposition of ZnO thin films

In this work, ZnO thin films with two different thickness (600 and 800 nm) were deposited at 95 °C from zinc acetate precursor using SILAR technique. The glass substrates were etched with diluted HCl and subjected to ultrasonic waves for 20 mninutes and then thoroughly cleaned with mixture of ethanol and acetone. ZnO thin films were obtained from three solution: cationic solution, anionic solution and complexing solution. Cationic solution (0.1M) and complexing solution (0.1M) were prepared by dissolving znic acetate dihydrate [Zn $(CH_3COO)_2.2H_2O$] and NaOH pellet, respectively in de - ionized water. The de - ionized water was used as a anionic solution. Perfectly cleaned glass substrates were dipped in cationic, complexing and anionic solution alternatively, for each cycle. After completion of dipping cycles, the substrates were dried in air. The deposition parameters employed in this study are displayed in table 1.

Table 1: Deposition parameters

Parameters	*Value*
Concentration of the cationic solution	0.1 M
Complexing agent solution (NaOH)	0.1 M
pH of the complexing agent solution (NaOH)	12
Temperature of cationic solution	32°C
Temperature of anionic and complexing solution	95°C
Dipping time in cationic solution	2 s
Dipping time incomplexing solution	2 s
Dipping time in anionic solution	6 s

2.2 Characterization

The thickness of the films was measured by KLA - Tencor Alpha step IQ surface profiler. Deposited films were characterized using powder X - ray diffraction (XRD),

spectrophotometer, scanning electron microscopy (SEM) with EDAX analysis. The structural properties of the thin films were analyzed with help of PANalytical – PW 340/60 X'pert PRO X – ray diffractometer. The surface morphology of the films was observed with help of Hitachi S - 3000H SEM. The optical transmittances in the range of 300 - 1100 nm were carried out using UV - vis - NIR double beam spectrophotometer (PerkinElmer Lambda 35). Photoluminescence spectra were recorded as a function of wavelength using Spectrofluorometer (450W, Jobin Yvon - FLUOROLOG - FL3 - 11).

2.3 Photocatalytic experiment

Photocatalytic activity of ZnO thin films was tested against methylene blue (MB) under 100 W UV lamp. Prior to the photocatalyst test, photocatalyst dimension 1 cm^2 was droped into the test tube which containing 40 mg/L MB aqueous solution. During the experiment, air was boubbled through dye solution to achieve adsorption - desorption equilibirium between dye and catalyst. At a certain period, adequate quantity of dye solution was taken out during the illumination and the concentration change of MB nm was analyzed using UV - vis bouble beam spectrophotometer (PerkinElmer Lambda 35) by measuring the absorbance at λ_{max} of 664 nm. The degradation efficiency was calculated using relation [15]

$$\eta = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the initial concentration of MB solution and C_t is the concentration of MB solution after t hours of exposure in UV irradiation.

3. Results and Discussion

3.1 Structural studies

XRD pattern of SILAR deposited ZnO thin film was obtained using CuKα radiation wavelength of 1.5406 Å and the XRD pattern is shown in Fig.1. The film showed pollycrystalline nature and exhibit structure of ZnO which is very good agreement with JCPDS crd no.36 - 1451 [16]. No other phases related to Zn $(HO)_2$ or other Zn compound are observed in the XRD pattern. The presence of (002), (101), (102) and (103) peaks in XRD pattern reveals the hexagonal wrutzite structure of ZnO thin film. The (002) peak is very stronger than the other peaks, indicating the crystallite predominently grown along (002) plane. The crystallite size of ZnO film was

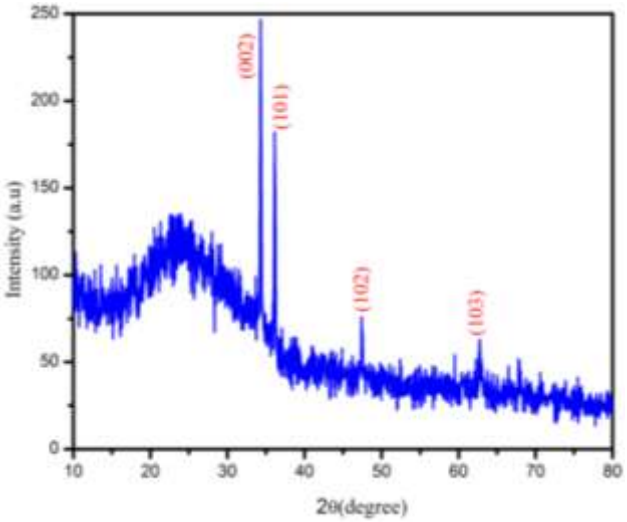


Figure 1: XRD pattern of ZnO thin film.

calculated using full width at half maximum (FWHM) of (002) peak using Scherrer's formula [17].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of X - ray used, β is the full width at half maximum (FWHM), θ is the Bragg's angle.

The lattice parameters '*a*' and '*c*' are estimated using the following formula [18, 19]

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

The crystallite size of the film is 43.58 nm and the lattice constants *'a'* and *'c'* are 3.2473 Å and 5.2062 Å, respectively. The estimated lattice constants are in good agreed with standard values (a = 3.2498 Å and 5.2066 Å). The calculated crystallite size and other structural parameters are revealed the SILAR deposited film having the good crystalline quality.

3.2 Optical studies

Optical transmitance spectra of ZnO thin film, prepared by SILAR technique at the temperature of 95 °C, are shown in Fig.2. The sharp absorption edge affirmed that the film with 600 nm thickness shows high crystalline nature while the absorption edge decreases gradually instead of being sharp when the film deposited with 800 nm. This modification in absorption edge indicates the thickness affect linear growth in crystallite. Besides, there is shift in absorption edge to the longer wavelengths. All the films show averge transmittance more than 60 % in visible region. More than 75 % optical transmittance is observed in the ZnO film with 600 nm thickness. The transmittance significantly decreased to 55 % for the ZnO film with 800 nm. The decrease in transmittance would be due to increase in scattering of photon by the crysatl defects and increase in photon absorption.

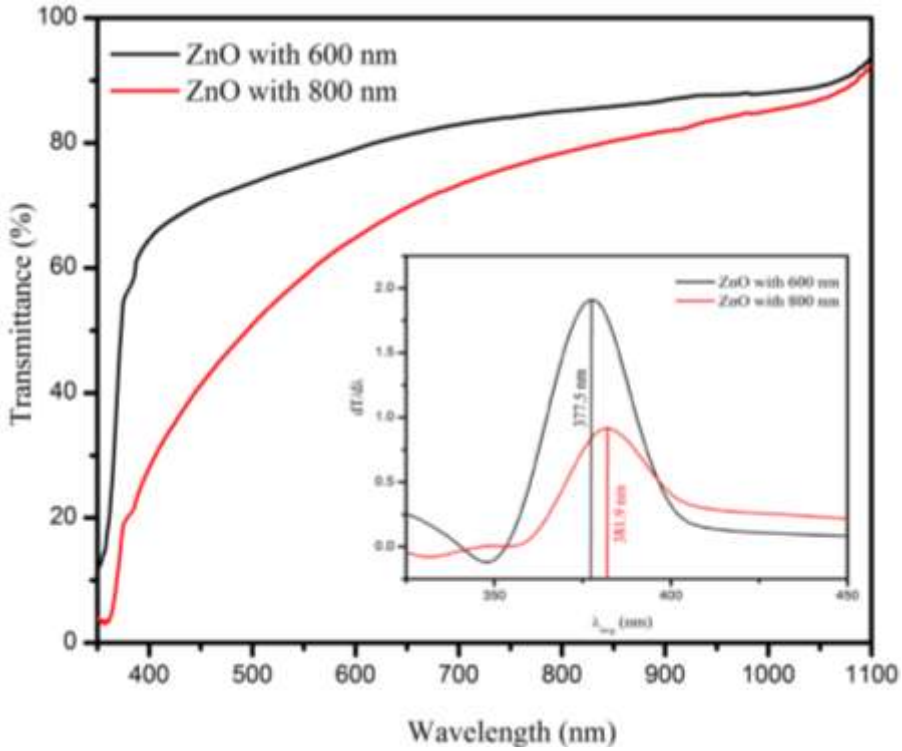
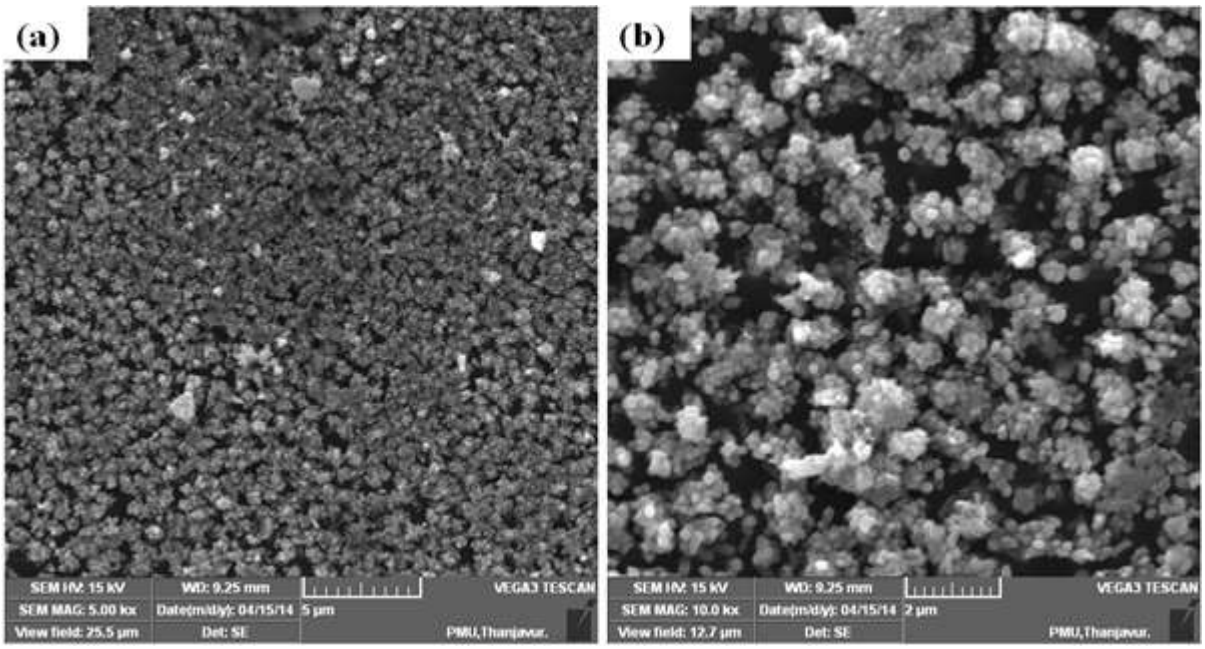


Figure 2: Optical transmittance spectra of ZnO thin films.

The optical band gap (E_g) of the films is calculated using first derivative of transmittance with respect to wavelength and the average Wavelength ($dT/d\lambda$ *vs.* λ_{avg}) shown in inset of Fig.2. The E_g value of 3.29 eV is observed for ZnO film of 600 nm thickness, while E_g value decreases to 3.25 eV for the film thickness of 800 nm. This decrease in E_g is not only ascribed to nano - crystal defects and also attributed to the effect of various factors such as carrier concentration, grain size, stoichiometry deviation and lattice strain.

3.3 Morphological studies and elemental analysis

Fig.3 shows typical SEM images of ZnO thin films. Fig.3a, 3b and Fig.3c, 3d are SEM images of ZnO films of 600 nm and 800 nm thickness for two different magnifications, respectively. These figures clearly show that there are changes in surface morphology of ZnO films with respect to thickness. For the film with 600 nm thickness, the film is consisting of porous surface of aggregation of small spherical grains, with average size of **50 nm** and separted by larger voids. More uniform and less porous surface of average **grain size of50 nm** is observed for the film deposited with 800 nm thickness. EDAX spectrum affirmed that the presence of anticipated elements such as Zn and O and is shown in Fig.4.



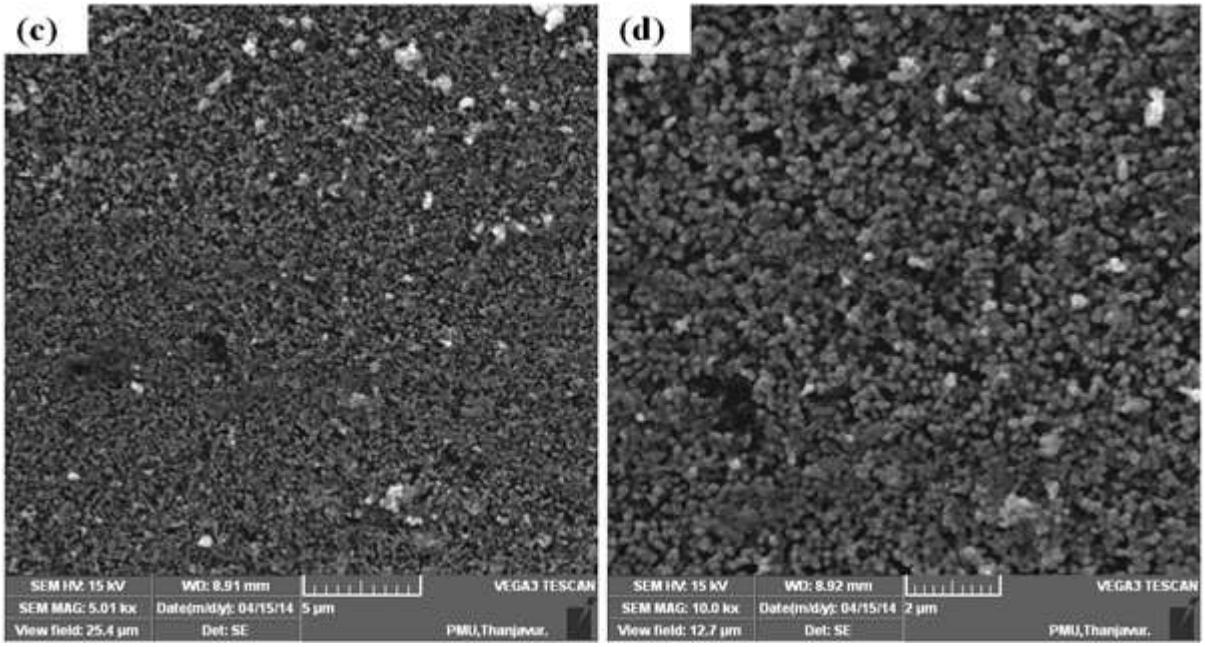


Figure 3: SEM images of ZnO thin films

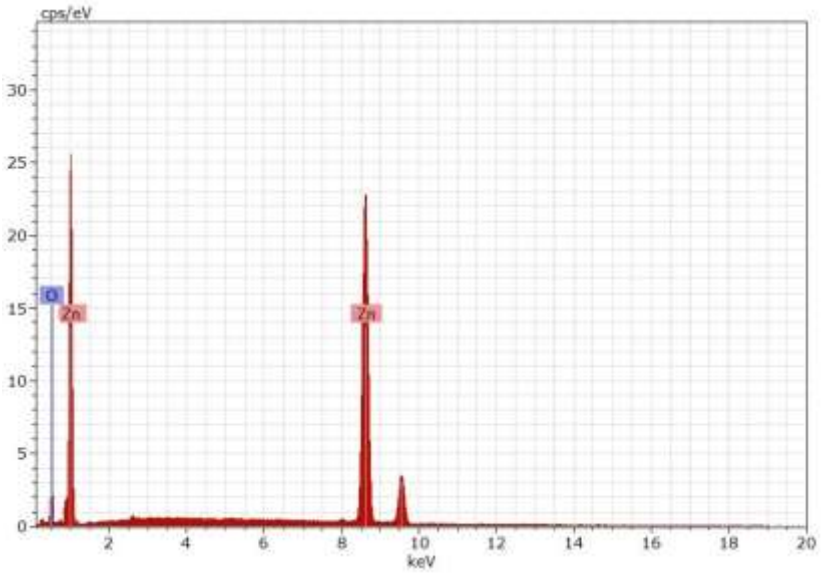
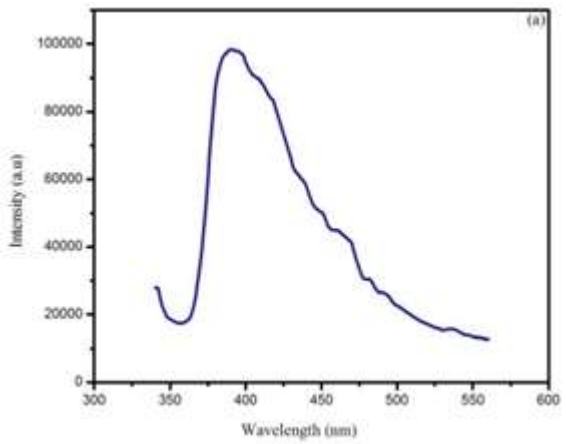


Figure 4: EDAX spectrum of ZnO thin film (600 nm)

Photoluminescence (PL) study

Photoluminescence spectra of ZnO thin films deposited with 600 nm and 800 nm thickness are shown in Fig.5a and 5b, respectively. The near band edge emission (NBE) of these films arises around 390 nm as expected [20, 21]. NBE caused by electtronic transition that occurred from conduction band to valence band. The redshift in NBE peak of 800 nm thickness films is observed and a supporting evidence for decrease in optical band gap obtained from the optical transmittance data. In addition, PL intensity of the ZnO film of 800 nm thickness is greartly lowered than that of film with 600 nm thickness, suggesting that the electron - hole recombination of the film becomes supressed upon increase in thickness of the film. This may lead to highest photocatalytic activity.



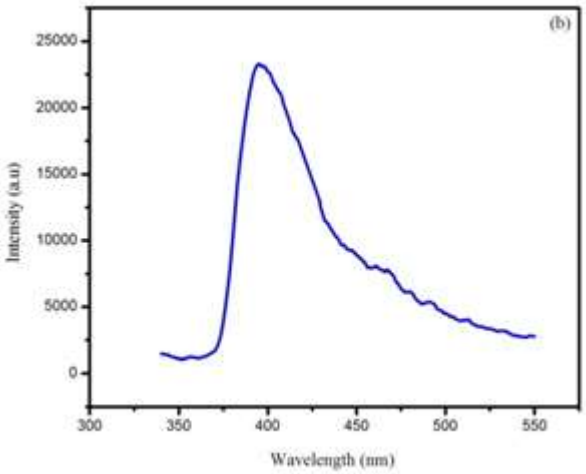


Figure 5 (a), 5(b): PL spectrum of ZnO thin film (600 and 800 nm)

Photodegradation of methylene blue (MB)

The catalyst activity of SILAR deposited ZnO thin films were studied by degradation of MB under UV light irradiation. Fig.6a and 6b display the UV - vis absorption spectra of MB solution with the 600 nm and 800 nmthickness catalyst upon exposing to UV light, respectively. MB solution shows characteristics absorption peak at 664 nm and used for varifying the photodegradation process of MB. The absorption spectra of MB solution were measeured in the presence of ZnO thin films at different time intervals. From the spectra, it is observed that the absorption peak decreased rapidly in the presence catalyst and UV light, which indicates photodegradation of MB. No progress in the reaction without ZnO catalyst was observed not shown in figure. The best photocatalytic activity of catalyst is attributed to the following reasons:

Generation of hydroxyl radicals ($OH^{\bullet}$) and superoxide anions (O_2^{-}), which are main responsible for degradation of dye molecules

The schematic representation of basic mechanism of photocatalytic activity of ZnO thin film is shown in Fig.7. According to the schematic representation, when the catalyst irradiated with UV light, electron - hole pairs are created on the conduction and valence band. These electron -

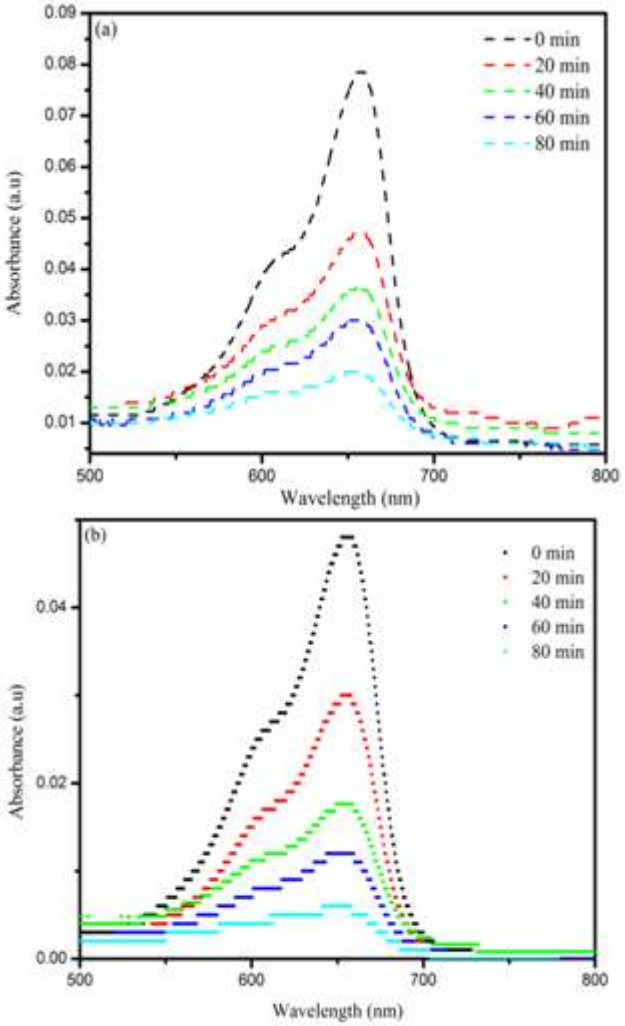


Figure 6 (a), 6 (b): Absorpton specta of MB solution in the presence of ZnO film (600 and 800 nm) at different intervals

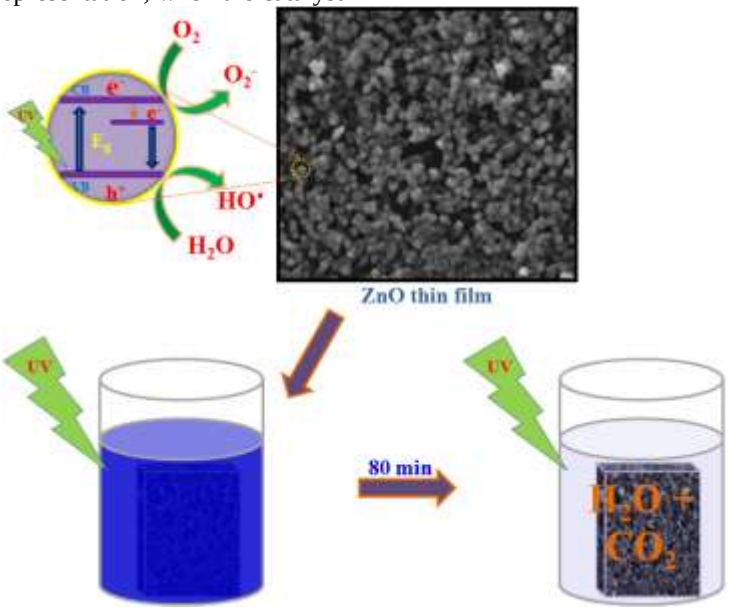


Figure 7: Schematic representation of photocatalyst mechanism of ZnO thin film

hole pairs are transferred to surface of the catalyst and then react withO_2 and H_2O molecules and a cosequence the following reaction takes placed in the reaction solution

$ZnO + h\nu \rightarrow ZnO (e^- + h^+)$

$e^- + O_2 \rightarrow O_2^-$

$h^+ + H_2O \rightarrow OH^{\bullet} + H^+$

$O_2^-/OH^{\bullet}$ + MB dye → intermediates → $CO_2 + H_2O$

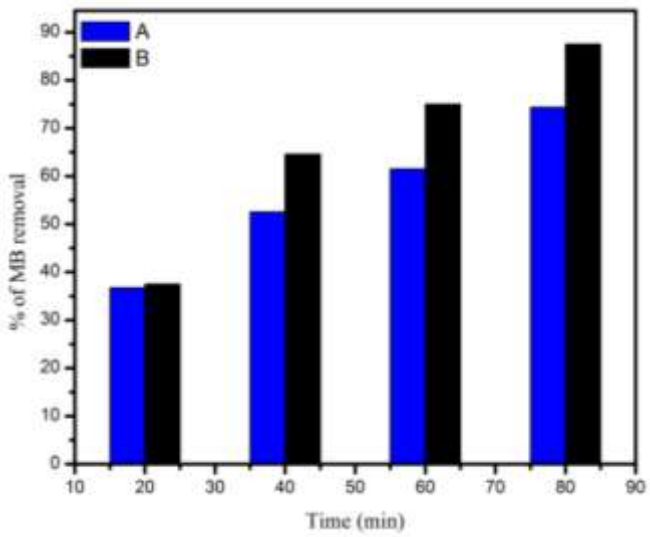


Figure 8: Photocatalytic degradation of MB using (A) ZnO film (600 nm) and (B) ZnO film (800 nm).

Tiny grains which lead to a more surface area and large active sites to the dye molecules

Role of irradiation time on photodegradation of MBwas evaluated to examine the photodegradation ability of ZnO thin films using UV light at different time intervals shwon in Fig.8. The results reveal that decomposition of MB increased linearly with increasing irradiation time. From the plots, it is noted that film with 800 nm thickness is more efficient at all reaction intervals. Decomposition of MB using 600 nm and 800 nmthickness filmswas reached 74.3 % and 87.5 % after 80 min irradiation time, respectively. Enhanced photocatalytic performance of film of 800 nm thickness could be ascribed to decreased electron - hole recombination rate as evidenced from the PL spectra. Under irradiation of UV light, electron - hole pairs are generated and then electron in conduction band of ZnO films can be traped by the surface defects, which significantly resists the charge recombinations. Besides, with increase of film thickness, the grain size decreased and increases the interaction between the film surface and dye molecules which enhances the photocatalytic activity of the ZnO film.

4. Conclusion

In this study, a simple and low - cost SILAR technique was used to deposit ZnO thin films onto the glass substrates with two different thicknesses (600 nm and 800 nm). The deposited films were characterized for their structural, optical and morphological properties. The structural properties exhibit the hexagonal wrutzite structure of ZnO and the crystallite size is 43.58 nm. The average transmittance of the films in the visible region is in the range of 55 - 75 % and the optical band gap 3.29 - 3.25 eV. The SEM morphology shows that the grain size is 50 nm with spherical shape. The ZnO film deposited with 800 nm thickness exhibits the best photocatalytic activity (87.5 % for 80 min) against MB dye degradation under UV irradiation.

5. Acknowledgments

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