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Effect of Annealing Temperature on The Improved Photo Catalytic Degradation of Zinc Sulfide Thin Films Under Visible Light Irradiation

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Abstract*: *Here, we reported a modern sort of zinc sulfide thin films as a catalyst was prepared from simple sol-gel approach. The as-deposited samples were further annealed at 200, 300, 400^0 C temperatures under atmospheric environment. The variation in the annealing temperature becomes crucial for optimizing the prepared samples characterization and dye degradation behavior. Structural and morphological analysis recommends that test were hexagonal crystal structure and spherical shaped morphology, particle size was found within the range of 25-40 nm. The significant red shift was found within the absorption edge and lessening of energy in the band gap was found whereas the annealing temperature is increased from 200 to 400 ^{o}C. Recombination of photo-generated electron-hole sets was moreover distinguished and the photo-degradation test was monitored methylene blue dye solutions under visible light irradiation. The 400 ^{o}C annealed sample showed superior photocatalytic performance such as high degradation efficiency and long term stability towards MB dye.

***Keywords*: ZnS; Annealing Temperature; Sol-Gel; Photo-degradation; Methyl blue; Visible light; Electron-hole separation.**

I. INTRODUCTION

Strong abilities and stable photocatalytic products tend to be developed to overcome global issues such as water emergencies and wastewater treatment. II-VI group semiconductor based photocatalyst show up as a competent invention in pollution control owing to their versatility, flexibility, controllability and easy production [1-3]. Since their significant properties of ZnS have taken tremendous consideration in photocatalysis, sun based energy transformation, and optoelectronics application. The varying annealing temperature is increases the significance to upgrade the ZnS properties for wide extend of applications [4-5]. Thin films are fascinated in the regions of photocatalysis and optoelectronics behaviors by electrical, optical and photo physical properties of the ZnS [6-7]. Generally, semiconducting based metal oxides such as TiO_2, WO_3, ZnO and SnO_2 [8-11] catalyst is very effective materials due to their suitable band gap, tunable electronic configuration, suitable physico-chemical properties and high absorption ability [12]. Recently, significantly improved interests have been focused on ZnS owing to its wealthy physical properties, such as magneto dielectric effect, quantum punctuations feature, magnetic properties and suitable optical and electronic configurations, lattice dynamics, and so on [13-15].Many works focuses on the ZnS structure, optical behaviors are how influence the photocatalytic performance, to our knowledge, reviews completely and methodically elaborating the structural, morphological, optical and photocatalytic behavior of annealed zinc sulfide thin films at different temperature are rare. Hence, we report a high performance visible light induced photocatalytic behavior of zinc sulfide as catalysts synthesized from sol-gel method.

II. MATERIALS AND METHODS

A. *ZnS thin film preparation*

The chemicals used in this study is Zinc Sulfate ($ZnSO_4.7H_2O$) as a source for Zinc, Thiourea (NH_2CSNH_2) as a source for Sulfide, and ultra pure water were the solvent and all the chemicals were without purification was further process. The sol-gel dip coating method adopted for the preparation of zinc sulfide thin films by using a microscopic glass as thin film substrate. 1:1 mole ration of $ZnSO_4.7H_2O$ and NH_2CSNH_2 source solution was prepared by using deionized water (100 ml) and magnet100 ml of deionized water and magnetically stirred 90 min. The resultant Sol was formed and it is treated slow evaporation for 1 hour.

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The substrate cleaning and coating process was followed by our previous published work [18] by using automatic dip coating unit with infrared dryer (Holmarc: HO-TH-02B) and the as-deposited class substrate were annealed at different temperatures like 200 ^{o}C, 300 ^{o}C, and 400 ^{o}C for 2 h in a muffle furnace to improve ZnS thin film crystallinity

B. *Photocatalytic activity set up*

Specially designed photocatalytic [20] setup was used evaluate MB dye degradation in this study.

A visible light source with a maximum performance of 500W Xenon light about 470 nm was used (Founded of Electric Light Source, Beijing). A specifically built quartz glass barrel (30 cm long and 40 cm long) is a part of the photocatalytic reactor. In a normal photocatalytic try, well surface covered (2x2 cm) ZnS thin film was immersed in 20ml of methylene blue dye fluid arrangement (5 mgL-1) in a Pyrex reactor. Earlier to illumination, the suspension was attractively blended for 1 h within the dim to reach the absorption–desorption harmony between color and the catalyst. The Hitachi UH5300 spectrometer was used to calculate the absorption spectra of dye degradation. The degradation efficiency was estimated based on the previous published work [16].

III. RESULTS AND DISCUSSION

A. *XRD analysis*

The phase nature for the prepared ZnS samples was distinguished by means of XRD design and the resultant graph is appeared in Figure 1. The as-deposited ZnS thin film is undefined in structure and no particular crystalline phase was identified. The ZnS thin film annealed temperature at 200 °C shows a measured increase in crystalline nature. The results clearly point out that ZnS thin film crystalline nature may be grown at annealing temperatures. This indicates that the pure phase was reached during the reaction process at the annealing temperature 400 °C. Entire exhibited peaks are can be assigned to the hexagonal ZnS structure and peaks are well matched with JCPDS data card no 80-0007 [17]. The XRD pattern revealed that no other impurities related to glass substrate is detected, which shows that the ZnS can successfully grown in hexagonal ZnS structure. It was clearly seen that the sharp seriously peaks was watched when the expanding the temperature. Moreover, the ZnS thin film catalyst calculated structural parameters are a=b=3.777 (Å), c=6.188 (Å) and Scherrer's equations has been used to determine the crystalline sizes [18] $D = K\lambda / \beta\cos\theta$, where crystallite size is *D*, shape factor is K which taken as 0.89, wavelength of the incident beam is λ, full width at half maximum is β and Bragg angle is θ. The grain size was estimated to be 25, 36 and 40 nm for 200, 300, and 400^{0}C annealed ZnS thin film respectively, which is calculated from FWHM value of XRD [19].

B. *Morphology and Elemental composition analysis*

Figure 2 (a-d) shows the FESEM images of ZnS thin film with different annealing temperatures. The surface morphology image shows foamy and porous with agglomerated particles for as-deposited and annealed at 200 ^{o}C ZnS thin films. The particles are virtually nano flake like morphology at 300^{o}C. In addition, increasing annealing temperature does not revise the ZnS thin film morphology but attractive the particles size and morphology was observed at 400^{0} C. It was clearly exposed that spherical nanoparticles sizes in the range of 25-40 nm was obtained. Figure 3 shows the EDAX spectra of 400^{0}C annealed ZnS thin film is composed of Zn (50.12%), S (48.65), along with Na and Si elements (1.23%), this small impurity are occurred due to elements of glass substrate.

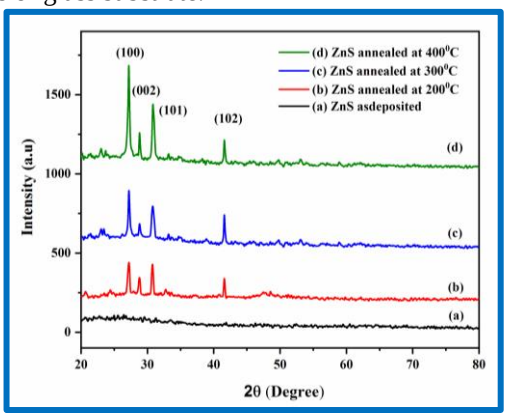

Fig. 1. XRD Spectra of prepared ZnS thin films

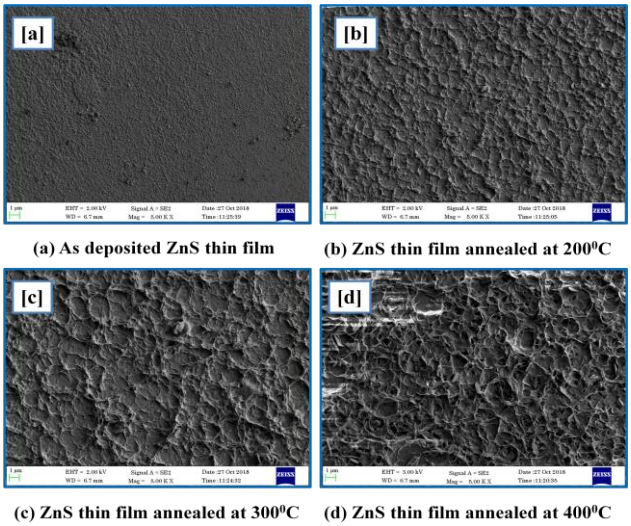

Fig.2. FESEM image of prepared ZnS thin films

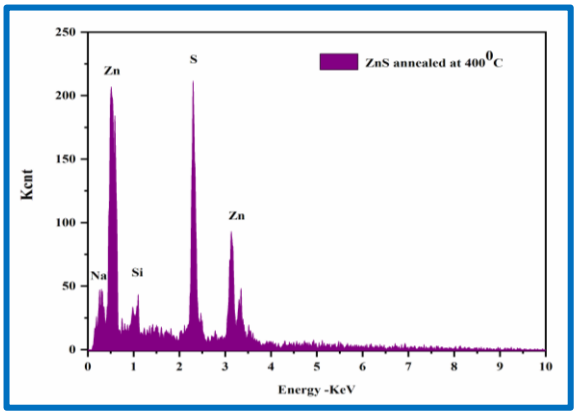

Fig.3. EDAX spectra of 400^{0}C annealed ZnS tin film

C. *UV-Visible analysis*

Optical properties of the prepared samples were evaluated by UV- Visible analysis and Fig. 4 exhibits absorption spectra of all the prepared samples. It was clear evident that the optical absorption maximum of ZnS thin film sample is originate to be 327 nm, auxiliary these bands were transfer to higher wavelength region such as 333 nm, 336 nm and 359 nm, respectively. This significant effect is due to the variation of particle size of the prepared ZnS thin films. The band gap energy was also found out using the Tauc plot [20]. The band gap energy was found to be 3.80, 3.73, 3.70 and 3.46 eV for as-deposited ZnS thin film, than 200^0 C, 300^0 C, and 400^0 C ZnS thin films respectively. Based on the reduction in the band gap energy the ZnS thin film annealed at 400 ^oC catalyst is more appropriate in the efficiency of photocatalyst than other ZnS thin films.

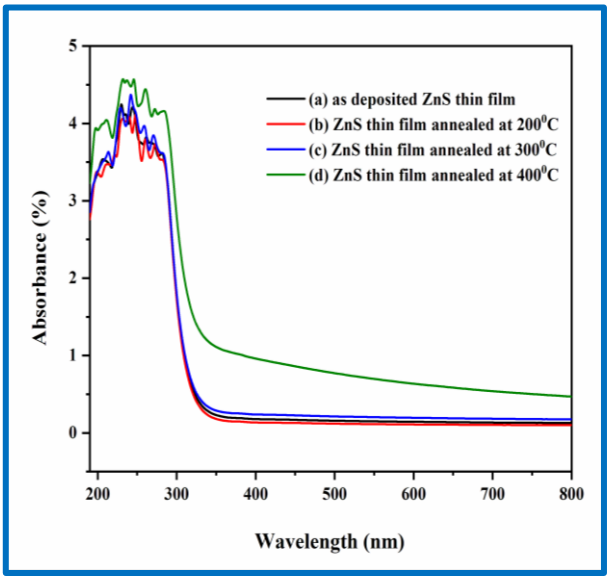

Fig.4.UV-Vis. Absorbance spectra of ZnS thin films

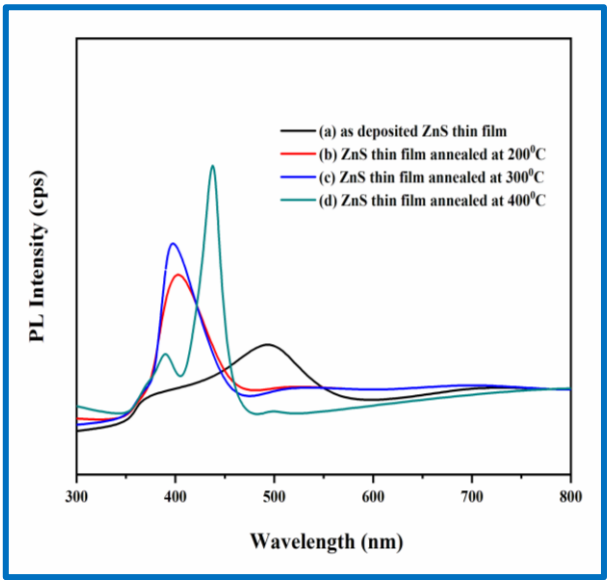

Fig. 5. Photoluminscence spectra of ZnS thin films

D. *Photoluminescence spectra*

Figure 5 [a] shows the room temperature photoluminescence spectra of all the prepared ZnS thin film catalysts. The spectra clearly exposed that the strong emission intensity appeared at 375-475 nm in the visible light region see Figure 5 [b], these findings shows that the obtained catalysts were more energetic in the visible light region. Further, this emission intensity of was steadily diminished after rising the annealing temperature (200 to 400^0C). This phenomenon was origin by the stifle the recombination rate of electron-hole pairs, which is encouraging for enhancing the photocatalytic performance.

E. *Photocatalytic studies*

Methylene blue dye absorption spectra of using the well surface covered (2x2 cm) ZnS thin film as catalysts. The absorption wavelength of MB was chosen for 621 nm and it can be consider as major peak for MB dye. After 180 min visible induced, the maximum absorption intensity was disappearing gradually. Moreover, color of the dye was become colorless after 180 min. light illumination. This could be due to the dye were oxidized under the visible light illumination. The dye removal efficiency of both dyes was evaluated for all the catalysts. Figure 6 shows the sequential degradation efficiency plot of MB dye under visible light irradiation. The results demonstrate that ZnS thin film annealed at 400^0 C catalyst shows significant enhancement in the catalytic behavior under visible light. The maximum MB dye degradation efficiency 79% was calculated for ZnS thin film annealed at 400^0 C catalyst. The order of the photocatalytic performance is 200^0 C > 300^0 C > 400^0 C. Hence, the stability test was carried out for MB dyes using the catalysts and the resultant graph is shown in Figure 7. After 5 consecutive cycle experiments, the catalysts were loss only 1.55% of removal efficiency from their initial degradation efficiency. Hence, the prepared fabrics show evidence of high stability and it can be useful for potential application for environmental remediation under visible light. The possible mechanisms for the photocatlytic degradation is under the visible light absorption of ZnS catalyst to create negative electron (e^-) and positive hole (h^+) charge sets, which are refereed as photo-excited state. At that point the energized photo created electron-hole match and created H_2 and O_2 are as a lessening and oxidation agent during the photocatalytic responses. Within the present case, the 400^0C annealed ZnS thin films catalyst only appear destitute catalytic execution than annealed ZnS thin films. This may be due to the speedy recombination rate of electron-hole combine and maintenance capacity of self-evident light due to the possibly tall band crevice vitality than annealed ZnS thin films, which is truly reduce the photocatalytic development. The moved forward photocatalytic component of the ZnS thin films annealed at 400^0 C catalyst is due to influence of temperature on the structural, optical and photocatalytic behavior of ZnS thin films that increase the crystalline size, which serve as an beneficial electron trap, subsequently maintaining a strategic distance from photo energized electron–hole recombination.

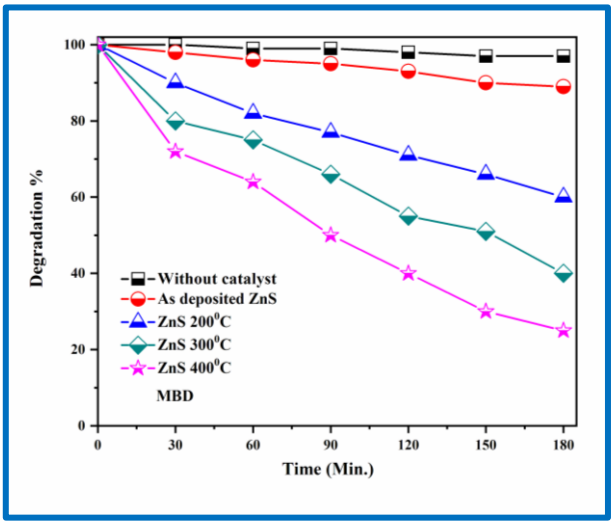

Fig. 6. Degradation efficiency of ZnS thin films

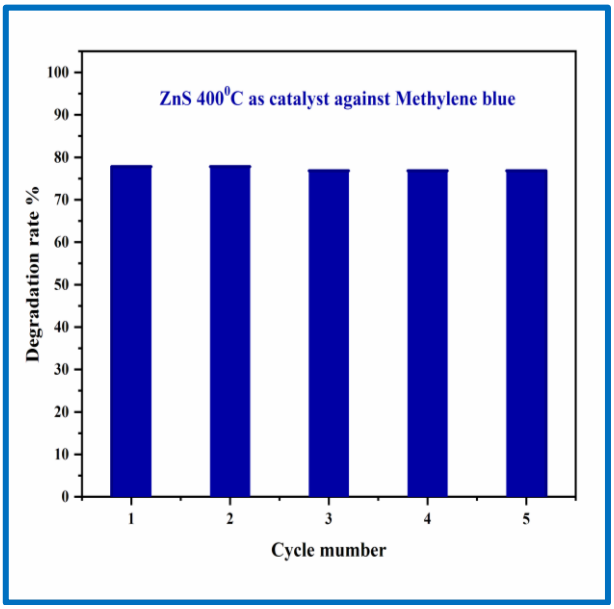

Fig. 7. Cyclic responce of ZnS thin films annealed at 400^{0}C

IV. CONCLUSION

In summing up, ZnS thin film catalysts were successfully prepared by facile sol-gel technique and the effect of temperature on the structural, morphological and optical properties were technically studied through various physic-chemical characterizations. The clear uniform spherical with hexagonal structure was identified by XRD, FESEM results. When the annealing temperature increases the band gap energy was drastically reduced from 3.80 to 3.46 eV. Moreover, prevention of recombination rate of the photo-generated electron-hole pair was also crucial to enhancing the photocatalytic behavior, which is studied by PL spectra. The photo-degradation test was monitored MB dye solutions and the 400^{o}C annealed sample showed superior photocatalytic performance such as high degradation efficiency (79%) and long term stability towards MB dye than other samples. This investigation concluded that degradation efficiency of ZnS thin films under visible light irradiation this is based on irradiation time, quantity and quality of the photocatalyst.

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