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Enhanced Photodegradation of Methyl Orange with ZnS Nanoparticles

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Abstract- In this analysis, ZnS nanoparticles have been synthesized by (2, 4 and 6 hours) different hours by solid state reaction method. The obtained ZnS nanoparticles have been characterized through XRD, FTIR, UV-Visible, PL, SEM and TEM measurements. The foremost intense broad peaks in the diffraction outline reveal the crystalline nature of prepared samples with the crystal size is approximately 3.68 nm. The optical bandgap has been evaluvated in the Uv-Vis. absorption spectrum which is found to be about 3.66 eV. The PL emission shows the blue green emission. SEM and TEM show the spherical shape of the ZnS nanoparticles. Photocatalytic activity of ZnS was evaluated by irradiating the solution of natural dye methyl orange (MO) in presence of solar light.

Keyword- ZnS nanoparticles, Photocatalytic activity, Methyl Orange.

I. INTRODUCTION

In recent years, Nano devices have substantially modified the optical,magnetic photocatlytic properties of nanotechnology, according to the study of intensive research for their use to create nano-devices [1]. Zinc Sulfide is a direct convertible semiconductor with a large band gap in the secondary and six semiconductors [2-3]. ZnS is an imperative mineral material for many types of applications, including optical finish, solid state solar cell windows, power optic converters, photoconductors, field effect transistors, sensors and light emitting diodes [4]. single or more nitrogen-tonerogens double bonds (N = N) are many times used in textiles, paper, leather, cosmetics and other industries.They are many times used in all shades, but their intermediate item, aerosol dyes and aromatic acids, toxins and toxins and humans for humans [5-7]. Recently, the abatement of waste to waste, biological degeneration and the electrochemical process to reduce various treatments. Process and photocatalytic degradation study,the photocatalytic method is solitary of the mainly determination of degradation technologies. biological compounds immediately and ultimately causes harmful carbon dioxide and water [8,9]. Photocatalytic procedure, photocatalytic reactions occur first when the target pollutant is absorbed on the exterior catalysis [10, 11]. The low density of organic pollution can enrich it by osurcaching photocatalytic efficiency. Therefore, photocatalist preparation is extremely essential with huge exterior area, improving the effectiveness of photocatalytic degeneration of organic pollution [12]. The solar photacalytic system is used to make orange oxidation in the chest. Many techniques are used to integrate ZnS nanoparticles chemical vapor deposition [13], wet chemical route [14], gas phase condensation method [15], co-precipitation method [16], solvothermal synthesis [17], hydrothermal process [18] thermal decomposition method [19] radio frequency magnetron sputtering technique [20] and solid state reaction method. These method is easy, simple, lowest cost and handy to perform Among that many researchers have analyzed the properties of ZnS nanoparticles into various method but only few researcher focused solid state reaction method. In these present work, Zinc sulfide nanoparticles are synthesized at different hours. The XRD, UV-Vis, PL, SEM, TEM, techniques have been adapted to characterize the synthesized ZnS nanoparticles and photocatalaytic activity.

Organization of this research papers done into five sections: Introduction, Related work, Materials and Methods, Results with discussion and Conclusions. Introduction section provides brief explain of present study.Various researcher studies on photocatalytic degradation of ZnS nanoparticles in related work section. Materials and methods sections contain precursors and chemicals for synthesized ZnS nanoparticles and characterization techniques employed for the analysis of ZnS nanoparticles by solid state reaction method. Results and discussion provides a brief on the characterization of ZnS nanoparticles and the analysis. Conclusion section provides the major conclusions drrawn from the results.

II.RELATED WORK

There are some reports on the enhanced photocatalytic degradation of methyl orange with ZnS nanoparticles. Some of the related works done by various researchers are, Zhiyuan Ye et.al.2018 [21] reported a comparative study of photocatalytic

activity of ZnS photocatalyst for degradation of various dyes. Fengjuan Chen et.al. 2013 [22] reported a facile route for the synthesis of ZnS rods with excellent photocatalytic activity. Mohd Mubashshir Hasan Farooqi et.al.2013 [23] Structural, optical and photoconductivity study of ZnS nanoparticles synthesized by a low temperature solid state reaction method. G. G. Ramteke.et.al.2018 [24] Structural and Optical Performance of ZnS Nanoparticles Synthesized via Chemical Route. P.P.Subha et.al.2015 [25] solar photo catalytic degradation of methyl orange dye using TiO2 nanoparticles synthesised by sol–gel method in neutral medium.

III.MATERIALS AND METHODS

A. Experimental

In this study, Zinc acetate dehydrate and thiourea is used to form ZnS nanoparticles. These chemicals were directly used without special treatment. In typical synthesis Zinc acetate dehydrate and thiourea are ground throughly. Finally mixed powder was transfer to crucible and powder was calcinated in a muffle furnace for 400^0C at different hours 2, 4 and 6h respectively. The prepared ZnS nanopowder is shown in Figure 1. This method was also adopted by Wang and Hang [26] to prepare ZnS nanoparticles.

B. Characterization of ZnS nanoparticles.

The crystal structure and phase of ZnS nanopowder were studied by X-ray diffraction analysis using SHIMADZUXRD 6000. The morphology of the samples was characterized by SEM (Hitachi S-4500 SEM Machine) and TEM analyses.The absorption spectra were measured using UV–Vis spectrophotometer (SHIMADZU-UV 1800). The PL spectrum was recorded on a fluorescence spectrophotometer with an excitation wavelength of 325 nm at room temperature.

C. Photocatalytic Experiments

Photocatalytic decomposition of Methyl Orange was examined by optical absorption spectroscopy. Degradation experiments be accomplish by adding 0.06g of ZnS in to 100 ml of 10 mg/lM aqueous MO solution. The assemblage was sonicated and stirred in the gloomy in order to reach adsorption-desorption symmetry amid MO and dissolved oxygen before irradiation. The stirred suspensions were then irradiated with sunlight, and 5.0 ml solution was drawn out in each 15 minutes. Then the deferral was kept under sunshine irradiation and the sample is taken-out for each 15 min (up to 75 min).Because of the degradation of the dye the colour of the deferral changes from dark to light orange and then became colourless. This graphical abstract describe in general handling processes of dye infected water using the ZnS nanoparticles as shown in Figure 2. The concentration of MO dye in the samples was purposive using UV–Vis spectrophotometer.

IV. RESULT AND DISCUSSION

A. Structural analysis

Powder X-ray diffraction patterns of pure ZnS nanoparticles synthesized at different hours (2,4 and 6 h) at constant temperature 4000C with miller indices (hkl) viewing the crystal family of planes for apiece diffraction peaks are predicted shown in Figure 3. The intense diffraction peaks emerge at about 2θ of 28.700, 47.900 and 56.620 analogous with those from (111), (220) and (311) orientations, respectively [27] this spectra displays relatively low intensity reflections with a good deal (220) and (311) plane with strong priority orientation (111) plane has exhibit cubic crystal structure and coordinated with common JCPDS (05-0566) values of ZnS compounds. The XRD peaks are significantly expanded due to the small crystal size [28]. The average crystalline level is 2θ and the full width (FWHM),(hkl) peaks using Debye–Scherrer relation, the crystal size calculations are carried out from the Debye–Scherer relation [29,30].

$$D=K\,\lambda/ß\cos\theta$$

where, D is the average crystallite size (Å), K is the shape factor (0.9), λ is the wavelength of X-ray (1.5406Å) CuKa radiation, θ is the Bragg angle and ß is the corrected line augmentation nanoparticles. The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal and was evaluated by using the relation.

$$\delta = \frac{1}{D^2}$$

where, D is the quantity of crystal derived from XRD data and n is the factor that is equivalent to the low dislocation density. The dislocation density increases from 9.3416 $X10^{14}$ line/m^2 to 9.7796 10^{14} line/m^2 for upto 4 hrs, dislocation density of Zinc Sulfide decreases due to an increase in hours (6h) about 9.1216 line/m2 has decreases is indicating imperfection in a crystal related with the dislocation of the lattice. Table 1.dislocation density of Zinc Sulfide decreases due to an increase in hours [31, 32].The microstrain ε_{hkl} in the synthesized sample was designed by using the relation [33].

$$\varepsilon = \frac{\beta\cos\theta}{4}$$

The lattice parameters a,b,c for the cubic structure can be determined by the following equation,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where h, k and l are the miller indices of the peak. The crystalline size of ZnS nanoparticles is specified in the Table 1 accumulated in three different hours. The calculated average lattice parameters were 5.4152Å, 5.4221 Å and 5.3958 Å nm. As the hours of precursors is increases lattice parameters are estimated to decrease. It can be perceive that 4 hours averaging a crystal size of 3.68 nm with the optimum and favorable parameter more than the other hours.

B. Optical absorption study

The absorption spectrum of prepared ZnS nanoparticles is described in three different hours (2,4 and 6 hours) as shown in Figure 4. All samples are on the edging edge of 418 nm [34].The absorbance co-efficient is premediated using the formula,

$$\alpha = \frac{2.303A}{l}$$

where, A is the absorbance and l is the path length. The value of optical band gap is gritty from the absorption spectra using the Tauc relation [35]

$$\alpha h\gamma = A(h\gamma - Eg)^n$$

where, α is the absorption co-efficient, A is the stable having detach worth for dissimilar transition, hγ is the photon energy and Eg is the band gap energy n depends ahead the nature of transition. The band interval is a negative number for n = 2, 3/2 and 3, so the relationship to the ZnS is n = 1/2, which confirms the permitted straight change. Figure 5. Curves of $(\alpha h\gamma)^2$ versus hγ for ZnS nanoparticles produced in different hours. Eg values are obtained directly by drawing the lines to the X-axis. The spacing of the energy gap measured from these layers is represented in Table 2. In this table, Eg values vary from ZnS nanoparticles to varying times from 3.41 to 3.83.Among the ZnS products, the nanoparticles with the pack at 6h reveal the high band gap energy. Therefore, it has been taken as an appropriate mix of further investigations. After the electronic absorption progression, electrons in maximum-energy states revert to minimum-energy states at the equal group at the equal position in the Brillonion region [36, 37]. Vibrating optical absorption margin and optical band interval energy are controlled.

C. Photoluminescent Spectroscopy

Photoluminescence is a vital tool to explore the quality of nanoparticles which depends on the size of the crystallites, morphology and chemical environment. PL Spectra of ZnS nanoparticles among different hours (2, 4 and 6 hours), excitation wavelength is around 325 nm as shown in Figure 6.In the Pl spectrum,two distinct peak was 422-487 nm[38-42]. The peak at 422 nm (blue) may be assign to the composition of the electrons from the conduction band and holes from the valence band. The emission green peak at 487nm can be connected with sulfur vacancy(s). The 2hrs of ZnS peak was expanded to compare with 4hrs and 6 hrs its indicating incorption of the samples.

D. Morphological Characterization

Using the SEM provided by EDX, Nanoparticles analysis ensured the metamorphosis, crystal size as well as structure for heavy ZnS, and confirmed their chemical structure. Nano-size ZnS grains are well defined mesopores shown in Figure 7(a).These micrographs make sure the highest intensity is growing. Besides the standardized allocation of particles, they have a cluster of particles or particles. An extremely brief survey of these pictures reveals the incidence of well-defined particles-spherical geometric particles. The most concise analysis of these pictures reveals the incidence of well-defined particles-spherical geometric shapes. The EDX analysis Figure 7(b) clearly showed elements like Zn and Sulfide. This color contains strong X-ray peaks with Zn Ka and S Ka, and we have noticed that atomic and weight percentage in Table 3. Zn and S are 40.34 at%, 24.91 wt% and 59.66 at% 75.09 wt% respectively.Figure7(c-e) surface occupancy plot (SOP) of the ZnS nanoparticles.

E. Transmission Electron Microscope

Morphological clarification was again confirmed via Transmission electron microscopy analysis. TEM is also worn for the size and crystallization model of particles are shown in Figure 8 (a and b). The particle size in ZnS nanoparticle is 3.68 nm. The shape of the particle is spherical shape and average particle size is 3.68 nm. The SAED method relates to the reflections of three strong crystal planes (111), (220) and (311), the particles are well segregated and proven by some integration [43].Any other variable rings absorbed into the SAED methods confirm the cubic ZnS at the crucial stage, which is a good deal with the XRD results (05-0566) in Figure 8c. The lattice space involving the two fringes was found 0.35 nm of ZnS nanoparticles in Figure 8d. The TEM image of nanoparticles clearly evident that the small nanoparticles are gathered together and having small size of nanoparticles.

F. Evaluvation of Photocatalytic activity

To further Photocatalytic mechanism, possible photocatalytic system of Methyl Orange dye through ZnS nanoparticles below solar radiation. ZnS nanoparticles made by the pair (e^-) hole (h^+) pair. At the topmost of the ZnS nanoparticles with spectroscopic radiation, e^- and h^+ can be caused by light radiation that can be seen by photovoltaic microorganisms, which are diluted with ZnS nanoparticles. The photocatalyze deoxidation procedure for ZnS nanoparticles can be compiled as follows from these principles and previous statements [21].

Electron hole pair generation

$$ZnS + h\gamma \rightarrow e^- + h^+$$

Surface trapping

$$h^+ + \equiv ZnOH \equiv ZnO^{\cdot} + H^+$$

electron –hole recombination

$$e^- + h^+ \rightarrow ZnS$$
$$e^- + \equiv ZnO^{\cdot} + H^+ \rightarrow ZnOH$$

Production of hydroxyl radicals

$$h^+ + OH^- \rightarrow .OH$$
$$e^- + O_2 \rightarrow .O^{2-}$$
$$.O^{2-} + 2H^+ + e^- \rightarrow H_2O_2$$
$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2$$
$$e^- + H_2O_2 \rightarrow .OH + OH^-$$
$$.O^{2-} + H_2O_2 \rightarrow .OH + OH^- + O_2$$
$$.OH + dye \rightarrow degradation\ produc$$

ZnS nanoparticles with huge surface area reaction increase due to the high adsorption of MO. The absorption is measured at 268 nm and 464 nm. Well-defined absorption strips were removed after 75 minutes in the occurrence of ZnS with sunlight [25].The degradation percentage (%D) of the MO dye can be calculated from the following equation,

$$\%D = \frac{C_0 - C_t}{C_0} X\ 100$$

where,% D is the degradation percentage,C_0 is the preliminary concentration, C_t is the After the radiation, the dye criterion is the favored time interval (0-75 min). Using the ZnS catalysis as a function of the wavelength (200-700 nm) of 0, 15, 30, 45, 60 and 75 minutes at various intervals of Figure 9 shows the absorption spectrum of MO. The absorption of MO, which is centered on 268 nm and 464 nm, had a disruption by monitoring the peak. The layers exhibit the highest absorption peak. The product of the ZnS catalyst in the degradation of MO dye results from 0 to 75 minutes from time intervals in Table 4.

G. Kinetic analysis

It is understand that the degradation of natural dyes by photocatalysts mostly follows pseudo first-order kinetics [44].

$$\ln\left({C_0}/{C_t}\right) = kKt = kt$$

Or

$$C_0 = C_0 e^{-kt}$$

where, k is the reaction rate constant, K is the adsorption co-efficient of the reactant. Relation curve between ln (C_0/C_t) and time (t) represents a direct line, the slope equals the noticeable first-order rate constant k. The kinetics of photodegradation of MO dye by ZnS nanoparticles were studied and the results are shown in Figure 10. According to the pseudo-first-order rate equation, the rate constant (k) for MO degradation by ZnS nanoparticles was determined.The plot of ln (C_0/C_t) as a function of irradiation time gives the rate constant value 0.0078 min^{-1} in Figure11.Moreover, the appropriate compatibility coefficient (R^2) is also determined to be 0.9963.

V. CONCLUSION

ZnS nanoparticles are successfully synthesized by simple solid state reaction method. The cystal size of the particles are determined using XRD results, the Strong preferred orientation along (111) plane and exhibit cubic type crystal structure. The crystal size is 3.68 nm. The optical bandgap has been evaluvated in the Uv-Vis. absorption spectrum which is found to be about 3.66 eV. The Photoluminescence emission range is 422-487 nm of both blue and green emissions. The SEM and TEM analysis also confirm their spherical shape morphology. EDX spectrum expressed to Zn and S stiochiometry. The photocatalytic performance of ZnS nanoparticles was evaluated using methyl orange dye as contamination compound. From the results, it has been found that the degradation rate of MO dye is solar irradiation on sunlight along with ZnS nanoparticles.

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Figure 1. Pure ZnS nanoparticles

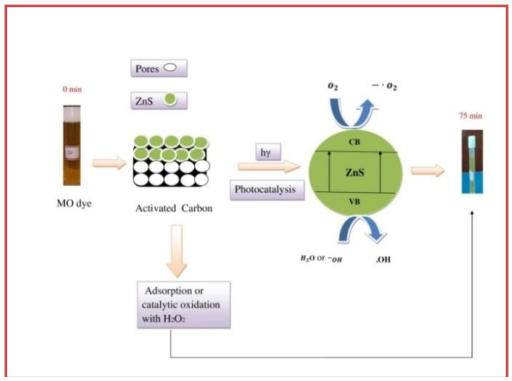

Figure 2. The graphical abstract of MO dye using ZnS nanoparticles.

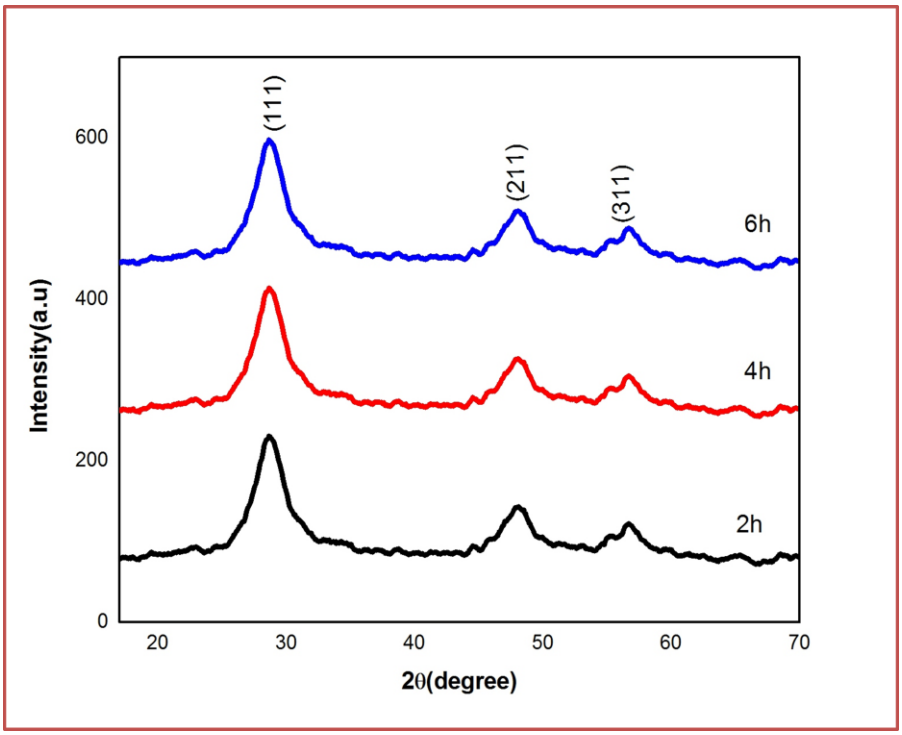

Figure 3. X-ray diffraction of ZnS nanoparticles at different hours

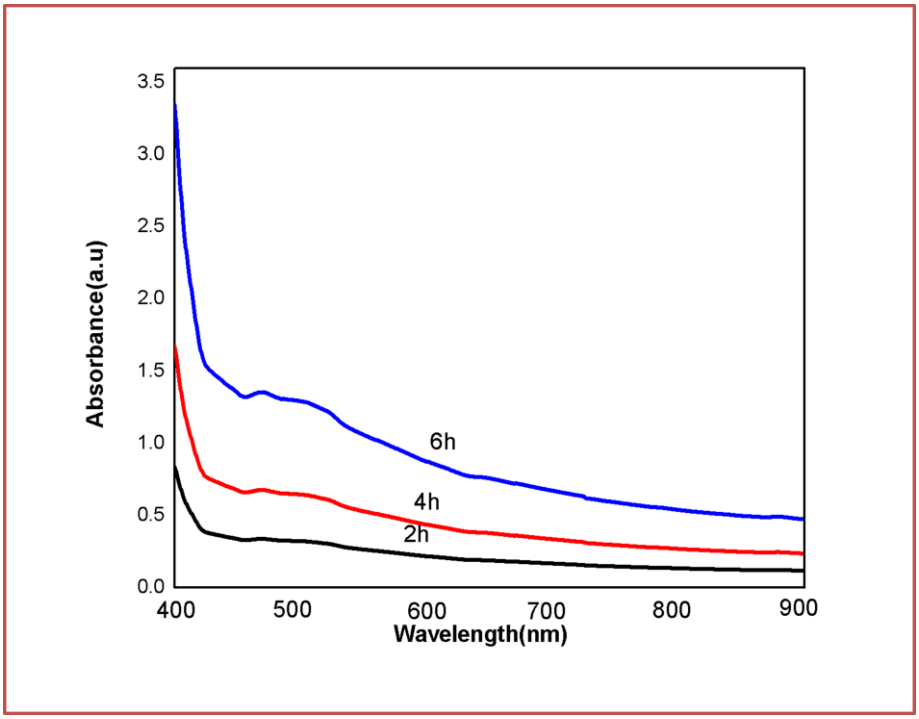

Figure 4. Optical absorption spectra of ZnS nanoparticles.

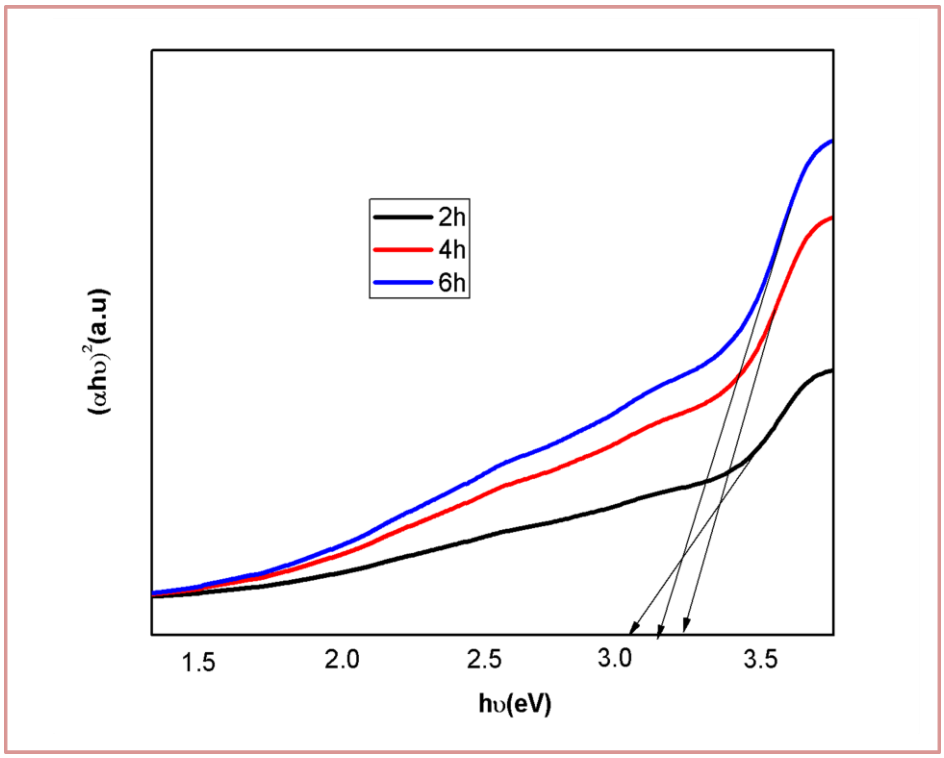

Figure 5. The plot of $(\alpha h\gamma)^2$ versus hγ for ZnS nanoparticles.

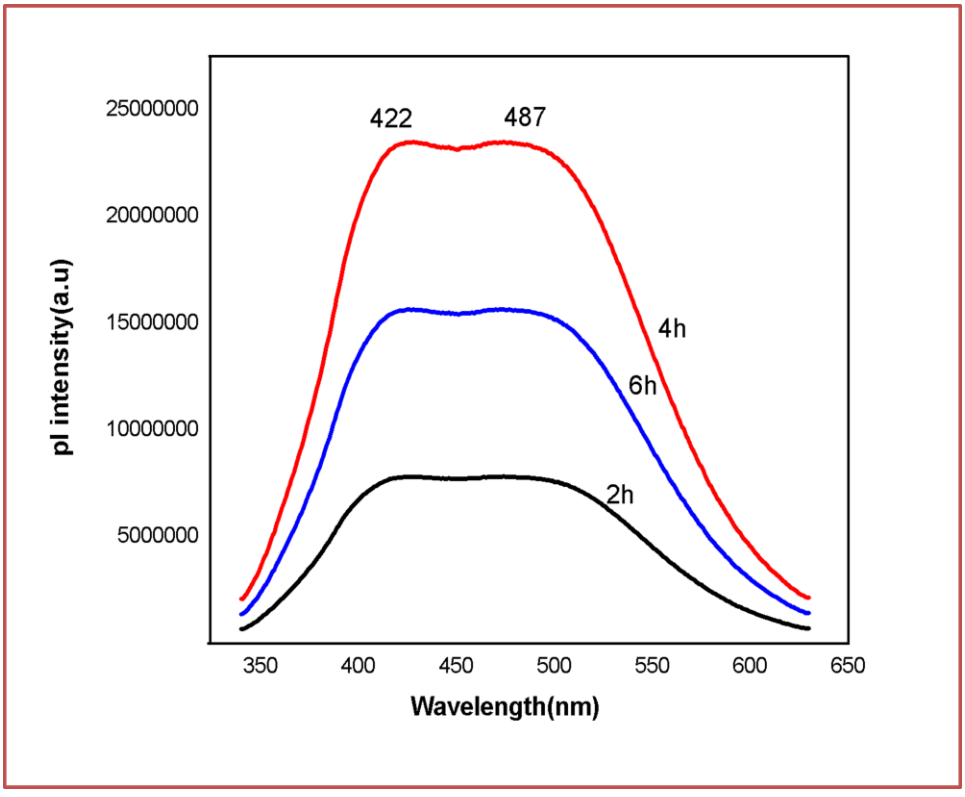

Figure 6. Photoluminescence emission spectrum of ZnS nanoparticles excited at 325nm

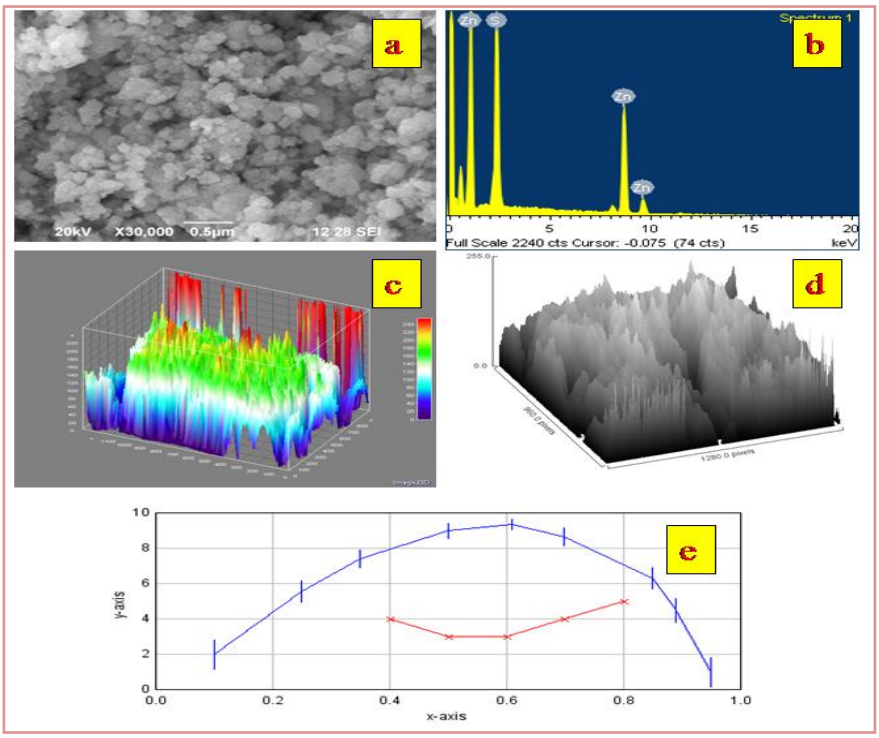

Figure 7 (a). SEM image (a) pure, (b) EDs spectrum and (c-e) Surface Occupancy Plot (SOP) ZnS nanoparticles.

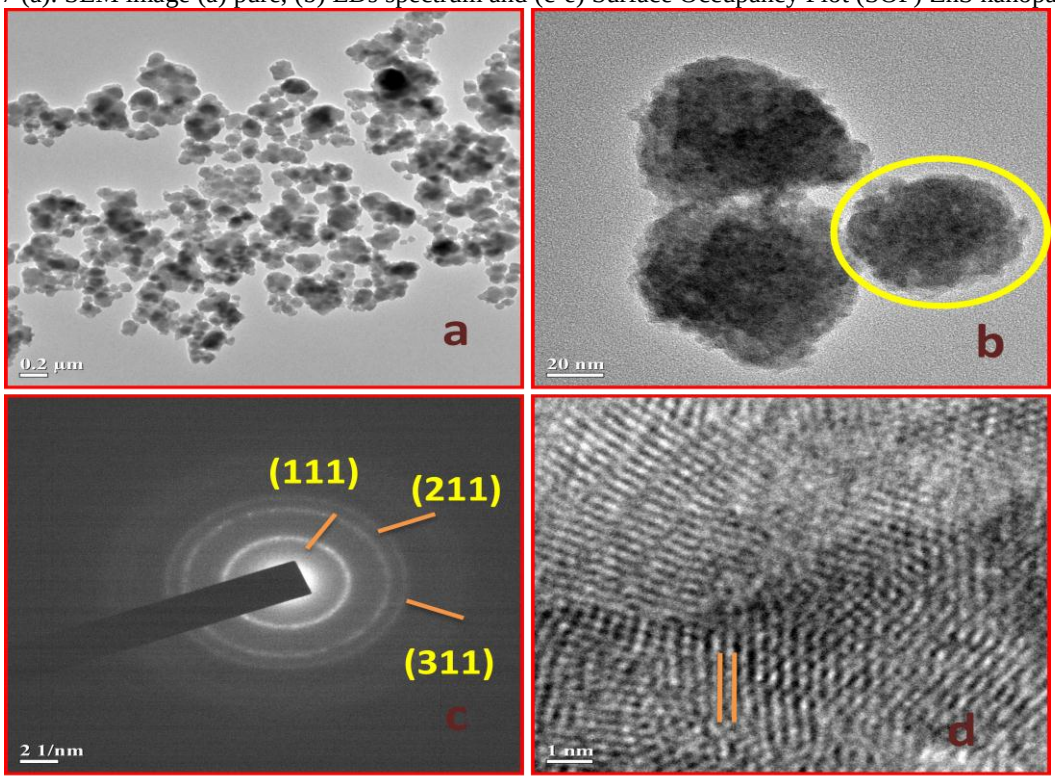

Figure 8. TEM images of ZnS nanoparticles (a–b), corresponding SAED pattern (c) and (d) frindge pattern.

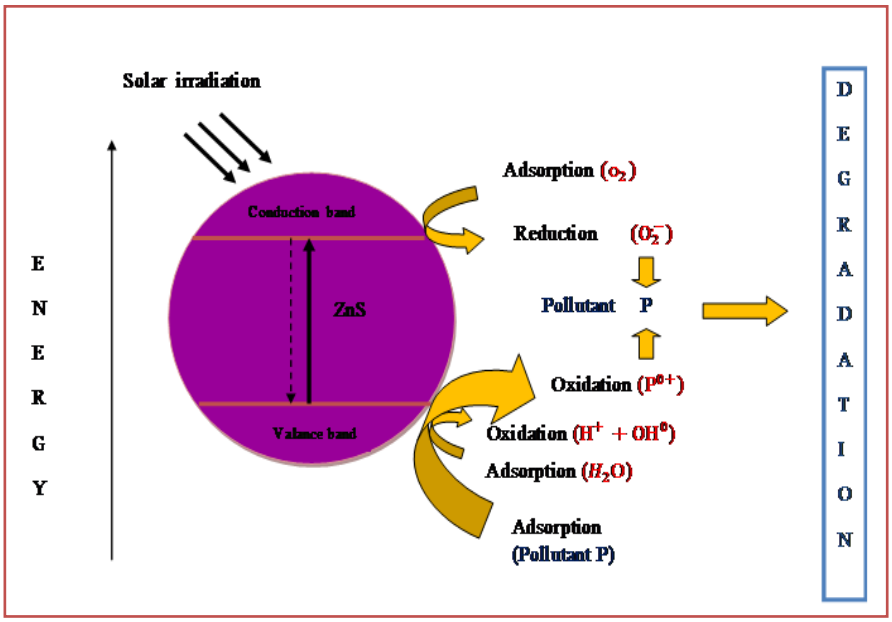

Figure 9. A possible photocatalytic mechanism for degradation of MO dyes by ZnS nanoparticles under solar light irradiation.

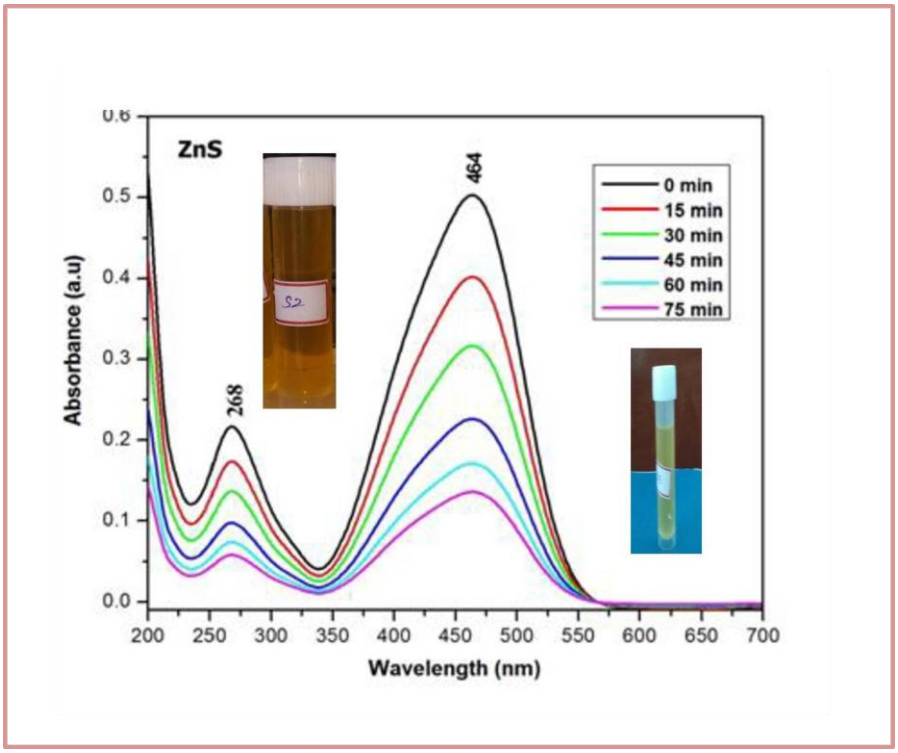

Figure 10. UV–Vis absorption spectra of MO with respect to irradiation time using ZnS Photocatalyst.

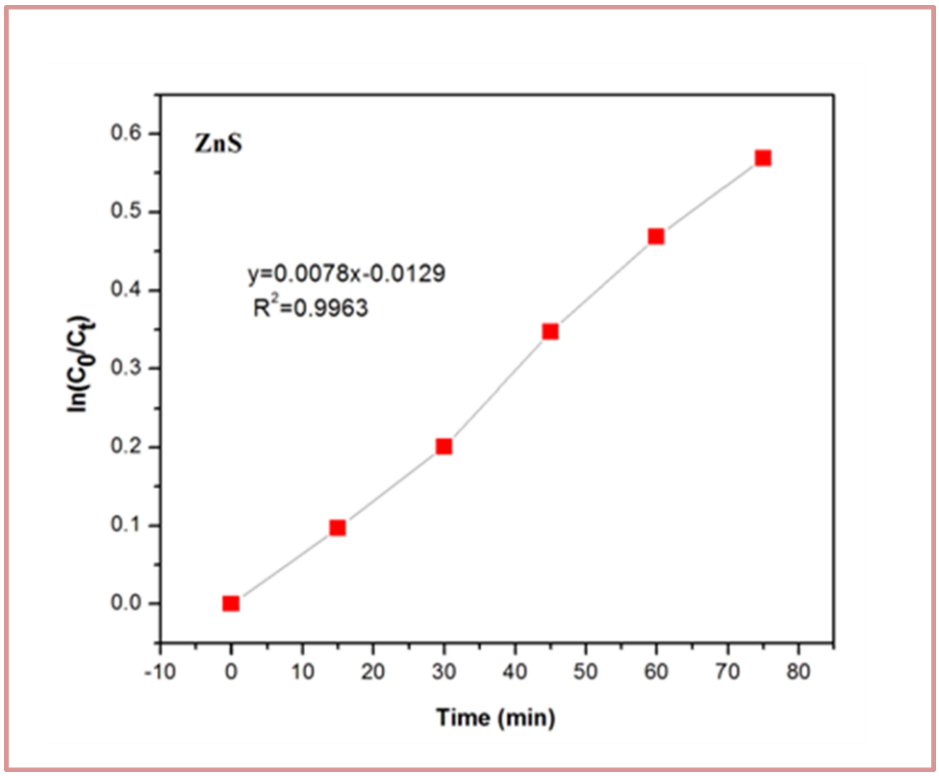

Figure 11. Relation curve between ln (C_0/C_t) and time (t).

Table 1.Structural properties of ZnS nanoparticles

Sample (hrs)	2ɵ degree	D space	FWHM	Cosɵ	Crystal Size (nm)	Average Crystal Size (nm)	Dislocation density δX10^{14} lines/m^2	Micro strain ε (x10^{-3})	Lattice Constant (Å)	Average Lattice constant (Å)
2	28.7083 47.9000 56.6250	3.1071 1.8975 1.6241	2.6167 0.9319 0.8803	0.9687 0.9319 0.8803	3.2717 3.7814 4.8313	3.97	9.3416 6.9943 4.2842	0.0110 0.0095 0.0074	5.4925 5.3669 5.3864	5.4152
4	28.3166 47.5375 56.4125	3.1492 1.9112 1.6300	2.7330 2.6750 2.1000	0.9696 0.9155 0.8812	3.1977 3.3879 4.4814	3.68	9.7796 8.7122 4.9197	0.1132 0.0106 0.0080	5.4545 5.4056 5.4063	5.4221
6	28.2916 47.4250 56.4125	3.1188 1.9055 1.6270	2.5833 2.4500 2.1250	0.9690 0.9146 0.8808	3.1103 3.6974 4.4290	3.81	9.1216 7.3145 5.0978	0.0109 0.0097 0.0081	5.4018 5.3896 5.3962	5.3958

Table 2. Calculated band gap energies of ZnS nanoparticles at different hours

ZnS	Band gap energy(eV)
2h	3.41
4h	3.66
6h	3.83

Table 3. EDX pattern of ZnS nanoparticles

Element	Weight percentage	Atomic percentage
Zn	24.91	40.34
S	75.09	59.66
Total	**100**	**100**

Table 4. The effect of methyl orange (MO) dye degradation by ZnS photocatalysts

Time (min)	% degradation of MO dye
0	0
15	20
30	36.99
45	55.00
60	65.99
75	72.99

AUTHORS PROFILE

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