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A study on effect of ligand on crystallography, morphology and photo-catalytic ability of ZnS nanostructures

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Abstract

A single source precursor zinc complex: Zn(phenyl alanine dithiocarbamate)$_2$ have been chosen to synthesize ZnS nanostructures by solvothermal route. Zn(phenyl alanine dithiocarbamate)$_2$ has been synthesized from ligand L-phenyl alanine dithiocarbamate (PHEDTC) by simple mixing. Crystalline texture, phase analyses and size-shape analyses of prepared ZnS nanostructures have been carried out by XRD and TEM, respectively. The hexagonal structure ZnS nanocrystals of various morphologies (nanosheets, nanotriangles and nano pyramids) have been confirmed by diffraction and electron microscope studies, respectively. UV-vis. absorption studies have been carried for the detailed optical analyses. Photoluminescence (PL) study was carried out to check luminescence of synthesized ZnS nanostructures in electromagnetic spectrum. It has been reported that morphology of synthesized nanostructures strongly depends upon the precursor complex prepared from ligand; L-phenyl alanine dithiocarbamate. Photo-catalytic potential of the ZnS nanostructures has been observed in visible light using MB dye as a pollutant in water medium.

Keywords: L-phenyl alanine dithiocarbamate (PHEDTC), Zinc Suphide, Solvothermal, XRD, TEM, UV-vis. Absorption Spectroscopy, Photoluminescence.

Introduction

A II-VI binary metal-chalcogenide Zinc sulfide semiconductor posses band gap (3.647eV) with various morphologies like nanorods, nanobelts, nanocombs[1-6] etc. ZnS nanomaterials have potential applications in the field of semiconductors like optoelectronics, photo-catalysis, bio-imaging, sensors[7-12] etc. Dithiocarbamates (DTCs) are the class of anionic ligands, which contain two sulfur donor atoms. These ligands stabilize the positive charge on metal ions towards the periphery of complex. The metal bis(phenyl alanine dithiocarbamate) complex have been known to be a precursor for the synthesis of nanomaterial, since they are easy to prepare, nontoxic and stable in nature[13-18]. Variation in derivatives of dithiocarbamate ligands in metal complexes remarkably effects the crystallography and morphology of metal-sulphide nanostructures[19].

In the present research work, solvothermal route of synthesis has been employed for the synthesis of ZnS nanostructures using single source precursor: Zn(phenyl alanine dithiocarbamate)$_2$. The photo-catalytic activity of ZnS nanostructures have been checked using MB dye as test pollutant in water.

Materials and methods

All the procured reagents were used without further purification. The analytical reagent grade chemicals: L-phenyl alanine ($C_9H_{11}O_2N$) (99.00%), zinc acetate $Zn(C_2H_4O_2)$ (99.50%), sodium hydroxide (NaOH) (98.00%), and ethanol (C_2H_5OH) (99.90%) were purchased from Spectrochem, PVT LTD. Mumbai (India), S D Fine Chem Ltd, Mumbai (India), Loba Chemie, Mumbai (India) and Changshu Yangyuan Chemical, China. The laboratory reagent grade chemicals: carbon disulfide (CS_2) (99.00%), methylene blue dye ($C_{16}H_{18}N_3SCl$) (99.00%) and diethylenetriamine ($N_3C_4H_{12}$) (98.00%) were procured from Loba Chemie, Mumbai (India) and Spectrochem Pvt. Ltd, Mumbai (India), respectively. Diethyl ether (C_2H_6O) required for synthesis was procured form Merck Pvt. LTD, Mumbai (India).

Preparation of L-phenyl alanine dithiocarbamate (PHEDTC): The synthesis route was according to the literature[20]. CS_2 (0.35 mL, 5.70 mmol) was added in 5 mL anhydrous C_2H_6O and cooled to 0˚C in an ice bath. $C_9H_{11}O_2N$ (936 mg, 5.70 mmol) and NaOH (456 mg, 11.4 mmol) were added in 10 mL anhydrous C_2H_5OH and added dropwise to the solution CS_2 followed by stirring for 3 h in an ice bath. The white solid was filtered and washed with Et_2O and dried in vacuum to yield PHEDTC as a pale yellow solid.

Preparation of Zn (PHEDTC)$_2$: Zn (PHEDTC)$_2$ has been synthesized by dissolving 25 ml water containing 5 mmol zinc acetate to 25 ml of water containg 0.01 mol PHEDTC ligand. Precipitation results immediately and stirring continue for 45 min, filtered and rinsed distilled water[21-22]. Figure-2 shows the schematic synthesis route of PHEDTC followed by synthesis of Zn(PHEDTC)$_2$ complex.

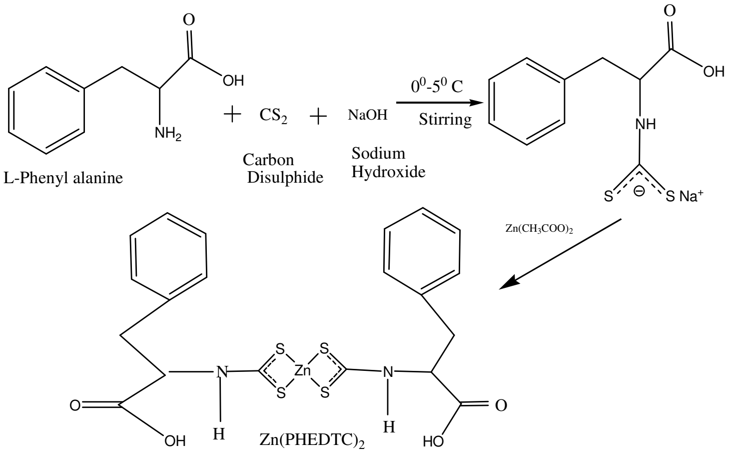

Figure-1: Schematic synthesis route of PHEDTC and Zn $(PHEDTC)_2$.

Preparation of ZnS Nanostructures: ZnS nanostructures were prepared from complexes Zn $(PHEDTC)_2$ via solvothermal route[23]. ZnS nanostructures were prepared by autoclaving 0.5g of Zn $(PHEDTC)_2$ in 15ml of diethylenetriamine at 170°C for 10 hours via the formation of intermediate complex as shown in Figure-3. The off white coloured product was centrifuged, filtered and washed with ethanol.

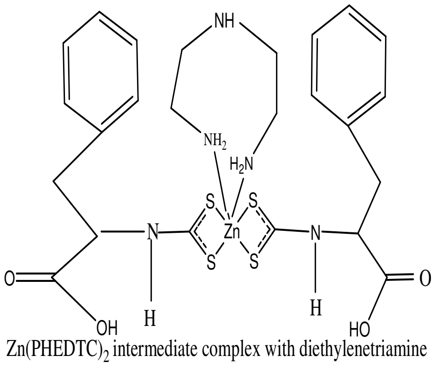

Figure-2: Intermediate Complex.

Characterization: The crystallographic analysis of synthesized nanostructures was done by powder XRD. The diffraction patterns were recorded in 2θ range of 20° - 80° using Rigaku Miniflex-600 Powder X-ray diffractometer. The transmission electron microscope (TEM) characterization for morphological analysis was carried by placing a drop of ethanolic solution of nanoparticles grid. The dried samples were analyzed on Hitachi (H-7500) electron microscope at accelerating voltage of 100 kV .The absorption spectra of synthesized ZnS nanostructures have been recorded in wavelength range 300nm-510nm, using Labtronics spectrophotometer. The emission spectra of samples were analyzed on RF-5301PC spectrofluorometer by dissolving in ethanol. The photo-catalyses ability of the synthesized nanomaterial was checked under UV light using MB dye as a test contaminant in water. The stock solution of dye was prepared by dissolving 3mg MB dye in 500 ml of water. Before illumination, the suspension of ZnS nanostructures (0.01g ZnS in 100ml dye solution) in dye was stirred in dark for 60 min for complete adsorption of dye on surface of ZnS nanostructures. After equilibration of solution, the suspension was illuminated with visible radiation for 105 min. During irradiation, the samples were collected within regular time intervals (15min) to analyze the photo-degradation of MB dye by UV-vis. absorption spectrophotometer in visible region (510-750 nm) of electromagnetic spectrum.

Results and discussion

Crystallographic analyses: XRD was carried out for phase determination. Figure-4 shows diffractogram of prepared ZnS nanostructures synthesized from zinc complexes. On Comparing the XRD pattern with JCPDS File No. 05-0492, it confirms the formation of hexagonal ZnS nanocrystalls. Diffraction pattern obtained as 2 theta positions; 28.57, 30.47, 41.12, 47.70.55.50 and 57.57 corresponds to crystal planes [100], [101], [102], [110], [103] and [112], respectively. The average crystalline size was calculated using Scherer formula as shown below.

$$D = {}^{0.89\lambda}/_{\beta cos\theta}$$

Where: λ is the wavelength of Cu radiation, ϴ is the Bragg diffraction angle and β is the full-width at half-maximum of the highest diffraction peak. The average crystalline size calculated as ~ 5.7nm. Such a small size was corresponds to peak broadening as shown in Figure-4.

Morphological analyses: The recorded TEM micrographs of ZnS nanostructures synthesized via solvothermal method shows that morphology of synthesized nanostructures varies from heterogeneous nanosheets to nanotriangles and nanopyramids which suggest that morphology of nanostructures can be tuned by varying type of ligand in precursors as conclude by Kaur B. *et al.*[24].

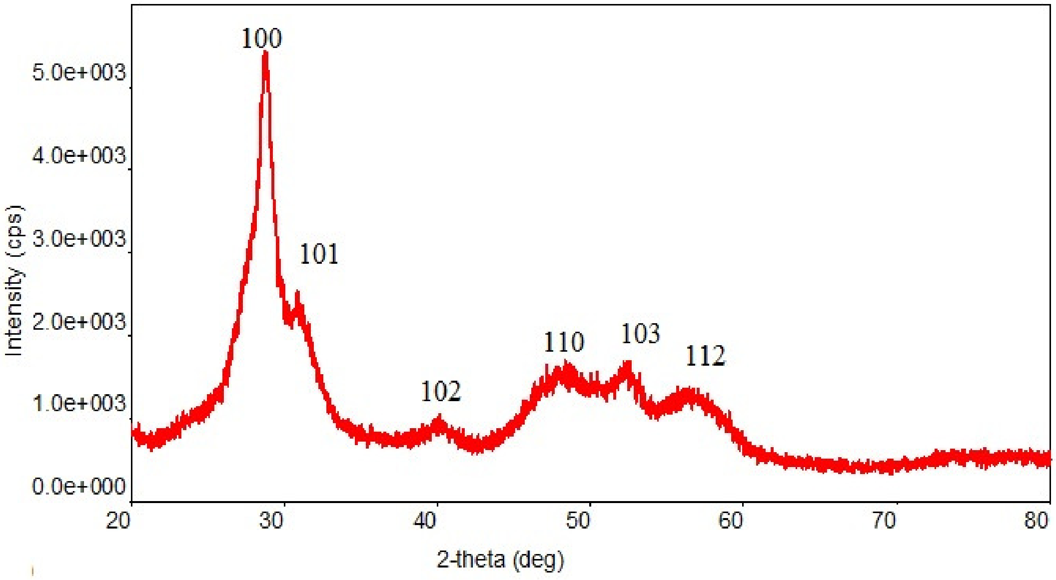

Figure-3: XRD patteren of ZnS nanostructures prepared from Zn(PHEDTC)$_2$.

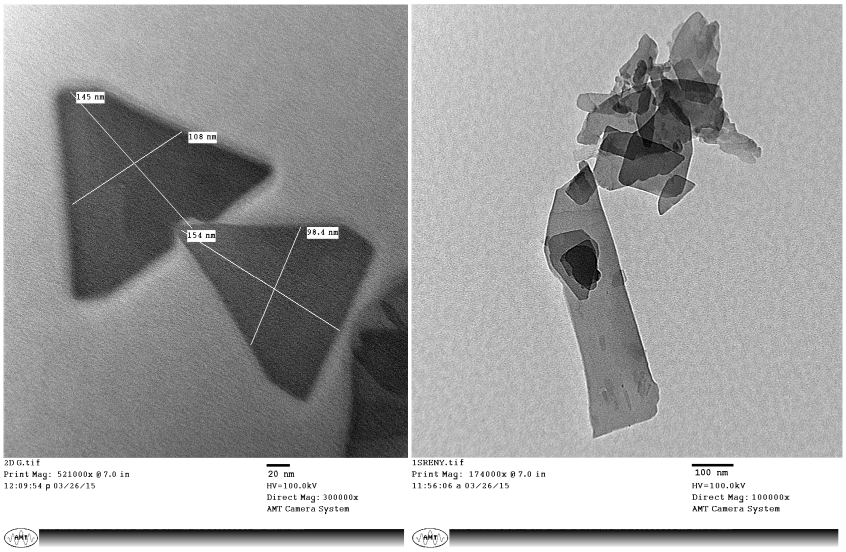

Figure-4: TEM micrographs of ZnS nanostructures prepared from Zn(PHEDTC)$_2$; (a) ZnS nanotriangles; (b) ZnS nanosheets.

The dimensions of nanostriangles and nanopyramids i.e length and width, calculated from TEM micrographs recorded for ZnS nanostructures are 95 nm and 24 nm respectively.

Optical analyses: The optical properties of nanomaterials can be monitored by UV-vis. absorption spectroscopy. The absorption spectra of ZnS nanostructures prepared from Zn (PHEDTC)$_2$ is shown in Figure-6. The recorded spectra of the synthesized nanostructures have broad absorption profiles in UV-visible region of electromagnetic spectrum, which makes these materials suitable for photo-catalytic applications.

Photoluminescence studies: Photoluminescence study provides valuable information about the transitions take place in nanomaterials. The semiconductor nanostructures have distinctive optical behavior. The room temperature PL spectra of ZnS nanostructures prepared from Zn (PHEDTC)$_2$ were recorded in the wavelength range 420 - 570 nm by exciting at 325 nm wavelength. Figure-7 shows the recorded spectra that PL emission band is highly symmetric and multiple peaks with broadening which demonstrating the participation of diverse emission centers in radiative processes. The ZnS nanostructures prepared from Zn(PHEDTC)$_2$ shows strong and symmetric emission peaks situated at 410 nm and 432 nm, which correspond to interstitial sulphur (I_S) lattice defect and interstitial zinc (I_{Zn}) lattice defect. A weak shoulder at 469 nm is assigned to dangling sulfur bonds in ZnS grains[25-28].

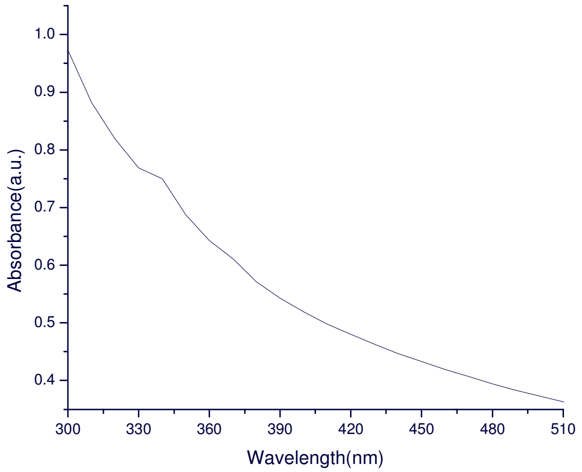

Figure-5: UV-vis. absorption spectra of ZnS nanostructures.

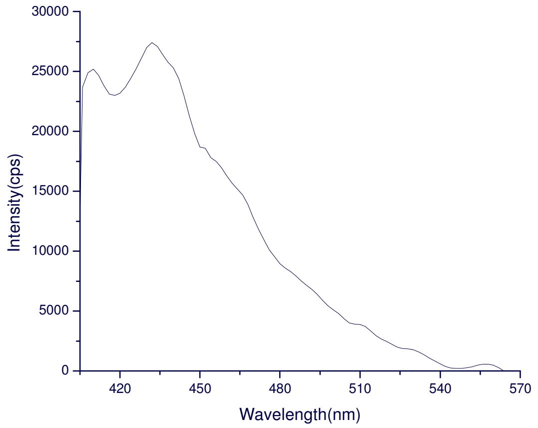

Figure-6: Photoluminscence spectra of ZnS nanostructures.

Photo-catalyses Mechanism: The degradation of added pollutant dye in water by synthesized nano photo-catalyst ZnS nanostructures was carried out under visible irradiation. When a visible light photon irradiate the synthesized ZnS nanostructures dispersed in MB dye contaminated in water, electrons(e^-) in the valence band jumps to conduction band, creating a positive charged hole (h^+) in valence band. Figure-8 represents the mechanism of various processes involved in photo-catalytic as well as photoluminescence of synthesized ZnS nanostructures. The two major possibilities either photo-generated $e^-$and h^+ can recombine leads to emission process or these can be trapped in defect states or transferred to the nanostructures surface. The holes in valence band react with the adsorbed H_2O molecules to form reactive intermediate $OH^{\bullet}$, whereas electrons in conduction band interact with dissolved O_2 to form $OH^{\bullet}$ radicals, which subsequently react with dye molecules lead to degradation to form simple products like water and gases. Photo-catalytic competence of ZnS nanostructures mainly depends upon number of generated $OH^{\bullet}$ radicals. Therefore, the production of $OH^{\bullet}$ intermediate will boost the tempo of photo-catalyses of pollutant.

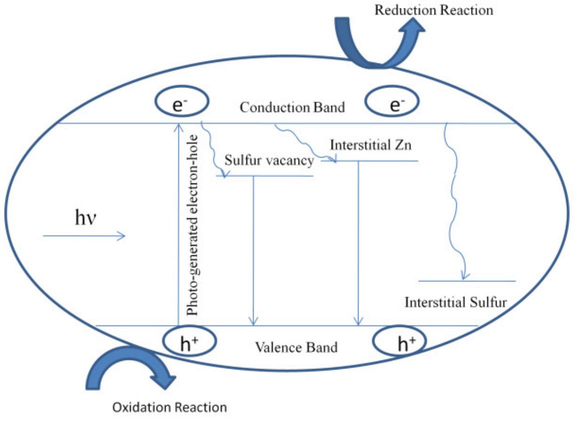

Figure-7: Presentation of processes involved in photo-catalyses and emission of ZnS nanostructures.

Photo-catalyses mechanism can by described as follows:

$$ZnS + h\nu \xrightarrow{\qquad} ZnS^{*}\,(h^{+} + e^{-})$$

The oxidation of water by holes $[H_2O \leftrightarrow H^+ + OH^-]$

$$h^+ + H_2O \xrightarrow{\qquad} OH^{\cdot}$$

$$O_2 + e^- \xrightarrow{\qquad} O_2^{\cdot}$$

The transient formation of hydroperoxide redicals:

$$2H_2O + e^- + O_2^{\cdot} \xrightarrow{\qquad} 2OH^{\cdot} + 2OH^-$$

Tantative degradation reaction between reactive intermediate & dye molecules

$$OH^{\cdot} + C_{16}H_{18}N_3SCl \xrightarrow{\qquad} CO_2 + H_2O + SO_4^{2-} + NH_4^{+}Cl^{-}$$

The design of MB dye is represented in Figure-9. The MB pollutant transfomation into simpler molecules like CO_2, SO_4^{2-}, NH_4^{+1} etc occurs after hetereocyclic and homocyclic ring cleavages as shown in Figure-10. After ring cleavages of MB dye, the complete minerlization of MB dye is done via various reactive intermediates like $OH^{\cdot}$ and $O_2^{\cdot}$ to easily removable and nontoxic gases and ions. The schematic photo-catalytic degradation pathways of MB dye by reactive free radicals has been described[29-31]. It is shown in Figure-10.

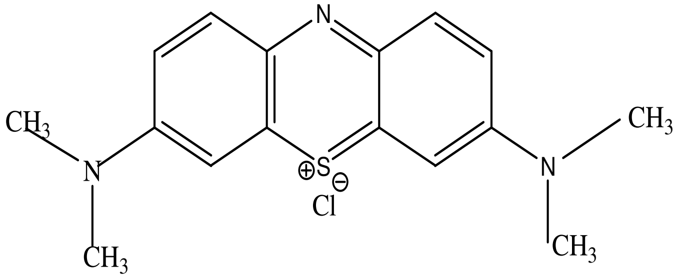

Figure-8: Methylene Blue.

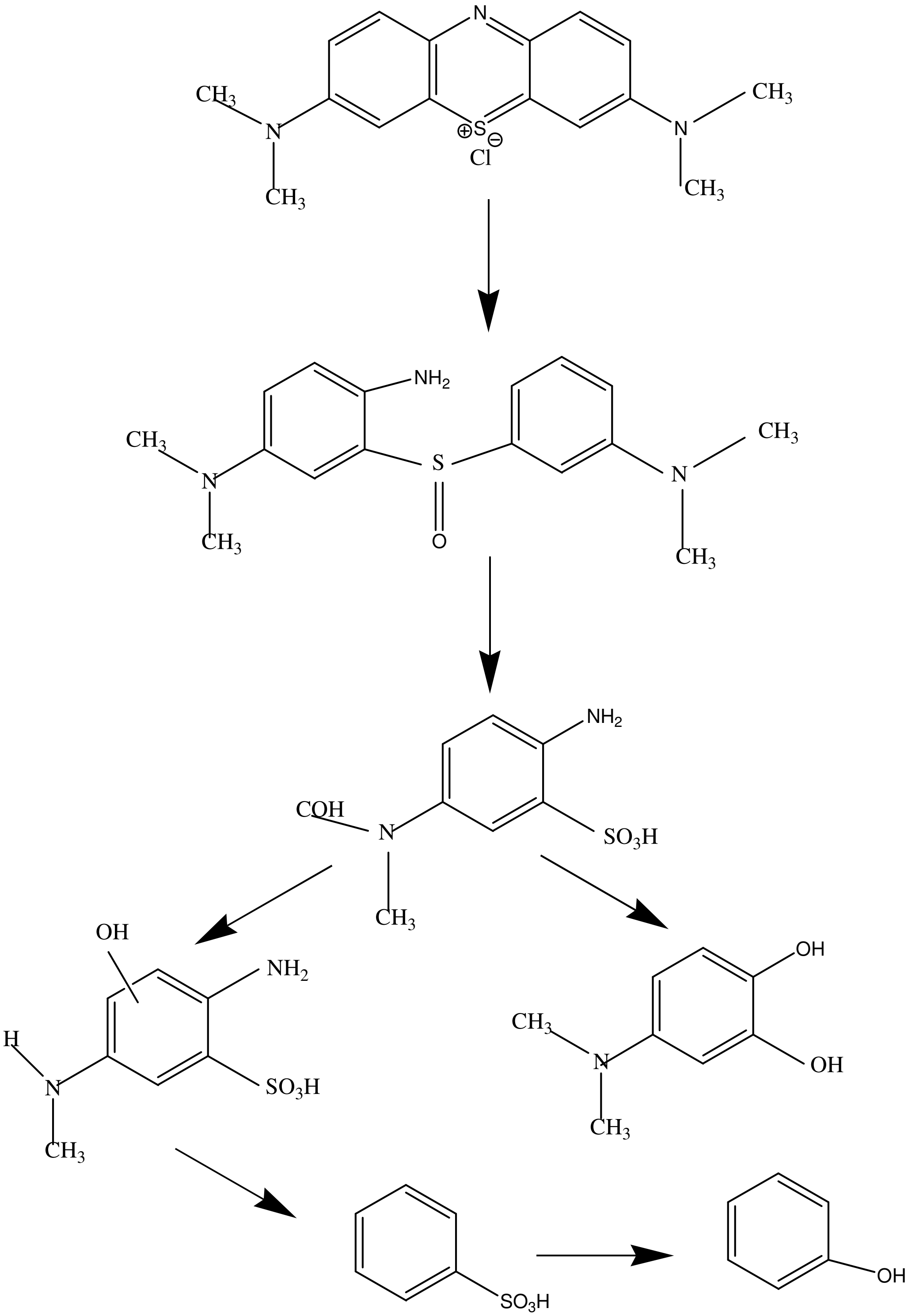

Figure-9: Degradation Pathways of MB dye.

The residual dye concentration v/s irradiation time was analyzed by UV-vis. absorption spectrophotometer. The decoloration of dye could be calculated using following formula:

$C(\%)= [(A_o-A)/A_o] \times 100,$

Where: C is the decoloration degree, A_0 and A are the absorption of dye solution before and after photo-catalysis, respectively. Figure-11 shows the spectra of MB dye for 105 min of irradiation on adsorbent ZnS nano photo-catalysts. The photo-catalytic efficiency basically depends upon the generation of photo-excited carriers followed by their surface transfer dominance over the radiative recombination. Pristine dye solution was also irradiated for 105 min. in radiation reactor to check the photo-bleaching of MB dye, but no photo-bleaching of MB dye was observed. Hence, the synthesized nanostructures are efficient photo-catalysts to degrade the MB dye.

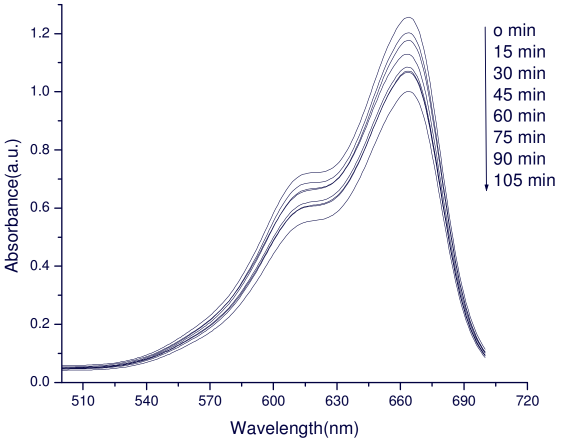

Figure-10: Spectra of absorbed MB dye pollutant for different durations under light.

Conclusion

Highly crystalline ZnS nanostructures have been successfully prepared from single source precursors Zn $(PHEDTC)_2$ by efficient solvothermal route. Mixture of nanosheets, nanotriangles and nanopyramids like morphologies have been formed in case of Zn $(PHEDTC)_2$ precursor. Synthesized ZnS nanostructures show symmetrical and broadened photoluminescence spectra in visible region of electromagnetic spectrum. Synthesized nanostructures seem to be efficient heterogeneous nano photo-catalysts for the degradation of aqueous pollutants.

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