Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2015, 6(8):25-29

Der Chemica Sinica
Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis of nano ZnS thin film by chemical bath deposition method and its application for the removal of Victoria blue dye

Sandip P. Patil[a], V. S. Shrivastava[a] and G. H. Sonawane[b*]

[a]*Nano-chemistry Research Laboratory, G. T. Patil College, Nandurbar(M.S.), India*
[b]*Deptartment of Chemistry, Kisan Arts, Commerce and Science College, Parola(M.S.), India*

ABSTRACT

Nanocrystalline thin films of ZnS are deposited using chemical bath deposition technique. Crystallite size of nanocrystalline film was determined from XRD data and was found to be 2 nm. The energy band gap of the nano thin film was determined from UV spectrograph, it was found to be 3.16 eV. The ZnS nano thin film was employed for the photocatalytic degradation of water soluble Victoria blue (VB) dye. Various parameters like pH, initial dye concentration and contact time have been studied and optimized. The optimum pH was 8 and equilibrium contact time was found to be 30 min for the photocatalytic degradation of the VB dye.

Keywords: ZnS; Nano thin film; Chemical bath deposition; Victoria blue; Photocatalytic degradation.

INTRODUCTION

Ever increasing industrial growth causes the increase in environmental pollution and it attained high level mainly in developing countries. Different types of industries discharges colouring matter through effluent which causes severe health problems through environmental pollution. These contaminants in water are not easily decomposable in nature. The untreated effluent causes cytotoxicity [1], genotoxicity and reduces light transmission through aquatic systems [2], they are responsible for increase in organic load and toxicity of wastewater [3]. Thus it is necessary to focus on reduction of environmental pollution. The conventional biological treatment methods are ineffective for removal and degradation of organics from wastewater [4]. Recent studies shows that, semiconductor based photocatalysis was found to be one of the promising technique for degradation of organics from wastewater [5-8]. Photocatalysis is mainly based on advanced oxidation process which produces hydroxyl radicals ($^{\bullet}OH$) and superoxide radical anion ($O_2^{\bullet-}$), which are responsible for photocatalytic degradation of dyes [9].

Thin films have gain gigantic importance due to their environmental applications. These thin films have low cost and higher energy efficiency. ZnS is used in two forms in photodegradation, either as suspended particles or as thin film. When ZnS is used as suspended particles in photodegradation then there is a problem of separation of ZnS after completion of reaction cycle [7]. Such problem could be avoided by ZnS thin film. ZnS thin film was the efficient photocatalyst used for photocatalytic degradation of different dyes[]. Various methods are employed for preparation of ZnS thin films like chemical bath deposition (CBD) [10,11], spray pyrolysis, physical vapour deposition, electrodeposition, magnetron sputtering[12], successive ionic layer adsorption and reaction (SILAR)[13]. Out of these methods CBD method was favourable due to its simplicity, convenience, low cost and reproducibility of large thin film area.

VB is a photosensitizer, which induce a cytotoxic response in several mammalian cell lines, though some dark toxicity observed [2]. VB causes eye irritation and on ingestion and inhalation shows hazardous effects.

Present study reports the preparation of ZnS thin film by CBD method and its application for the removal of Victoria Blue (VB) dye and optimization of parameters for removal VB by photocatalytic degradation.

MATERIALS AND METHODS

2.1. Materials

Victoria Blue is a cationic dye with molecular weight 506.08g/mol (M.F.$C_{33}H_{32}N_3Cl$). Stock solution of 500mg/L of VB was prepared in distilled water. Stock solution was diluted with distilled water to get, experimental solutions of desired concentrations. Other chemicals, zinc acetate dihydrate, thioacetamide, ethylenediamine (A.R. Grade) procured from Loba Chemie India Ltd. and used without further purification. The molecular structure of VB is shown in Fig. 1.

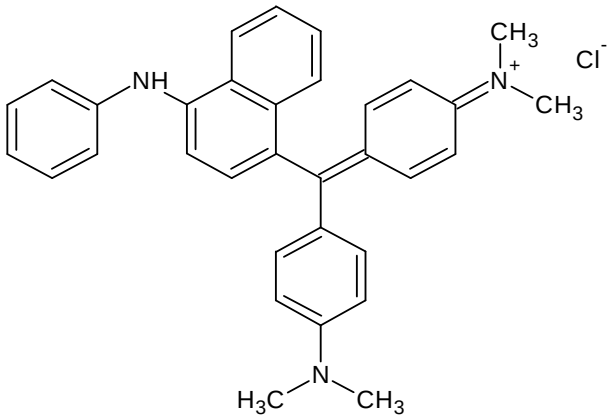

Figure 1. Molecular structure of the Victoria Blue

2.2. Preparation of ZnS thin Film

Commercial glass slides are used as substrates are first cleaned by detergent, then sulfochromic acid solution followed by deionized water. Glass substrates then dried in an oven. The deposition solution was prepared by first mixing 5 mL of 1M $Zn(OCOCH_3)_2{\cdot}2H_2O$, 20mL of 0.5M ethylenediamine, 30mL of 0.5M thioacetamide, then resulting solution was diluted upto 100mL by distilled water. Finally pH of the solution was adjusted to 6 by HCl solution [11]. Then cleaned glass substrate was mounted vertically in solution for 90 min at 25^{o}C. After complete formation of film, the substrate was removed from the bath and washed with distilled water and then air dried.

2.3. Photocatalytic study

The photocatalytic degradation of VB was carried out in photocatalytic reactor containing 400W mercury lamp. Cooling water jacket is used to maintain the temperature inside the reactor, which avoids the excessive heating of reaction mixture. 50mL dye solution was kept in contact with the ZnS thin film into reaction vessel placed in photocatalytic reactor. Desired amount of sample was withdrawn after regular intervals. Then changes in dye concentration were determined after centrifugation using UV-visible double beam spectrophotometer (Systronics model-2203) at λ_{max} 616nm. The percentage removal of VB can be calculated by equation 1,

$$Removal\ percentage = \left(\frac{C_o - C_t}{C_o}\right) 100 \qquad (1)$$

where C_o (mg/L) and C_t (mg/L) are the initial VB concentration and the VB concentration at time *t* respectively.

RESULTS AND DISCUSSION

3.1. SEM analysis

Morphology of ZnS thin film can be studied by Scanning electron microscopy (SEM) Figure 2. shows the SEM of ZnS thin film. SEM micrograph shows the ZnS thin film formed is uniform, does not contain any cracks.

3.2. X-ray diffraction analysis

The XRD diagram of ZnS thin film is shown in Fig. 3. The prominent ZnS peaks are observed at 2θ of 22.2^o, 37.5^o, 43.7^o [14]. Crystallite size of nanocrystalline film determined by Scherrer equation was found to be 2 nm.

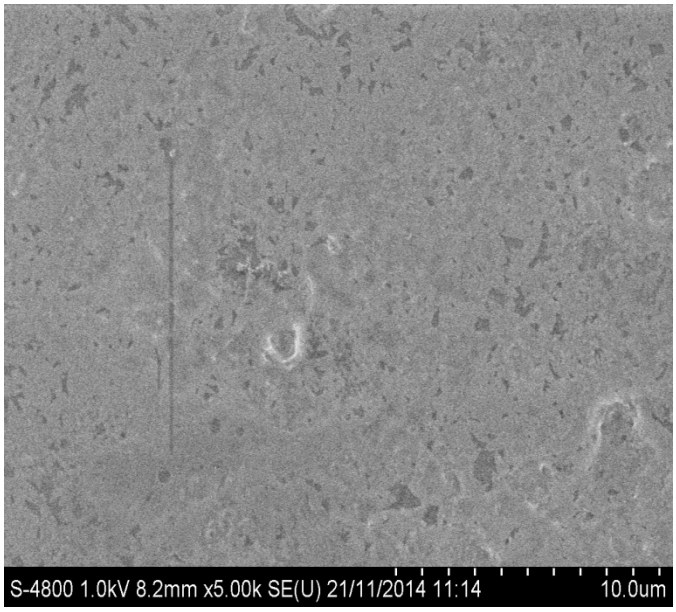

Figure 2. The SEM micrograph of ZnS

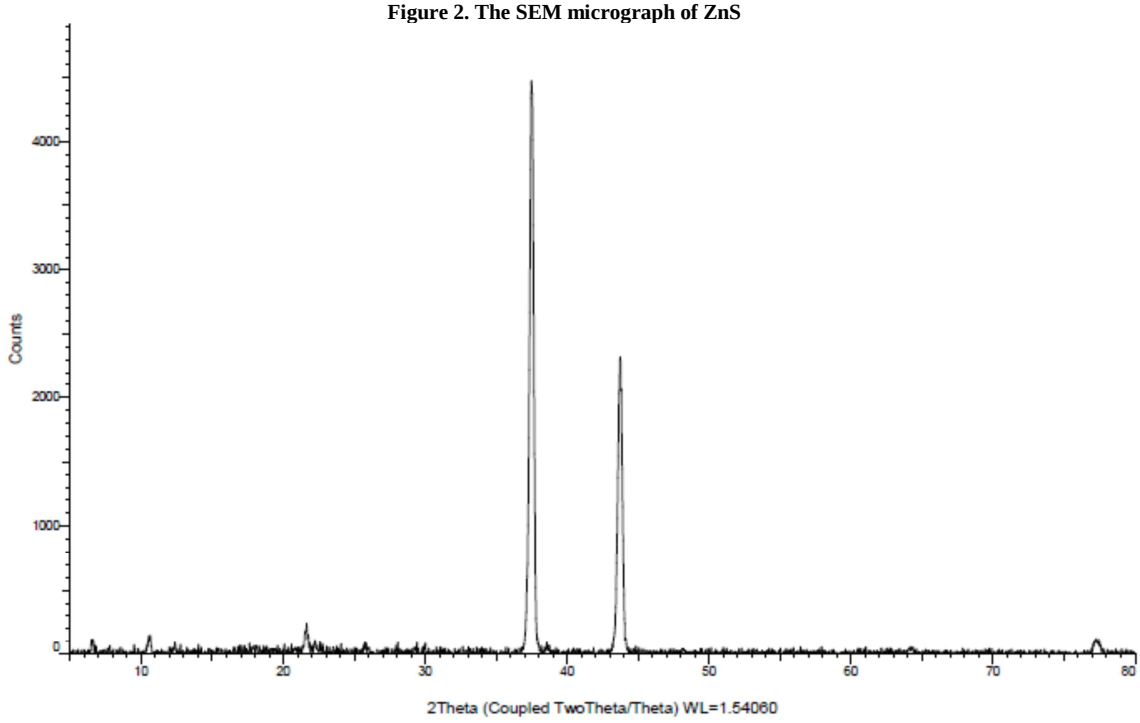

Figure 3. XRD diagram of ZnS

3.3. Effect of pH

Photocatalytic degradation of dye significantly depends on pH of the dye solution. The effect of pH on photocatalytic degradation was studied from 1 to 10 at 100mg/L initial dye concentration. It was observed that percentage removal for pH 1 was 5% which increases upto 35% at pH 8, then it again decreases down to 27.5% at pH 10.

3.4. Effect of contact time and initial dye concentration

Contact time and initial dye concentration plays important role in photocatalytic degradation of dye. The rate of photocatalytic degradation of VB by ZnS thin films was studied at different dye concentrations from 100 to 400mg/L at pH 8. Figure 4 shows the effect of contact time on percentage removal of dye. Initially as time increases upto first 30min then thereafter it attains the equilibrium. The equilibrium time was found to be 30 min. At equilibrium time the percentage removal increases from 35 to 97.5% as dye concentration was increased from 100 to 400mg/L.

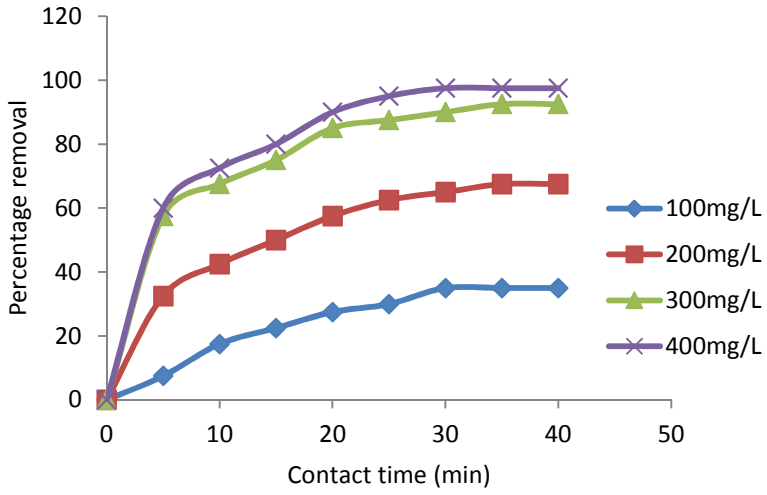

Figure 4. Effect of contact time and initial concentration of VB on percentage removal; pH 8

3.5. Optical studies

The optical transmittance spectra and absorbance spectra of ZnS thin film was studied in wavelength range 325-700 nm. The nature of transition during absorption was studied by relation between absorption coefficient α and photon energy hv [15] as,

$$\alpha\, hv = A\,(hv - E_g)^n \qquad (2)$$

where A is consant, E_g is band gap energy, hv is the photon energy, n is ½ or 2 for direct or indirect transition. Nature of transition takes place in ZnS thin film was determined from plot of $(\alpha hv)^2$ versus hv as shown in Figure 5. The straight line portion of the graph was extrapolated to the hv axis at $\alpha = 0$. The band gap energy was found to be 3.16eV.

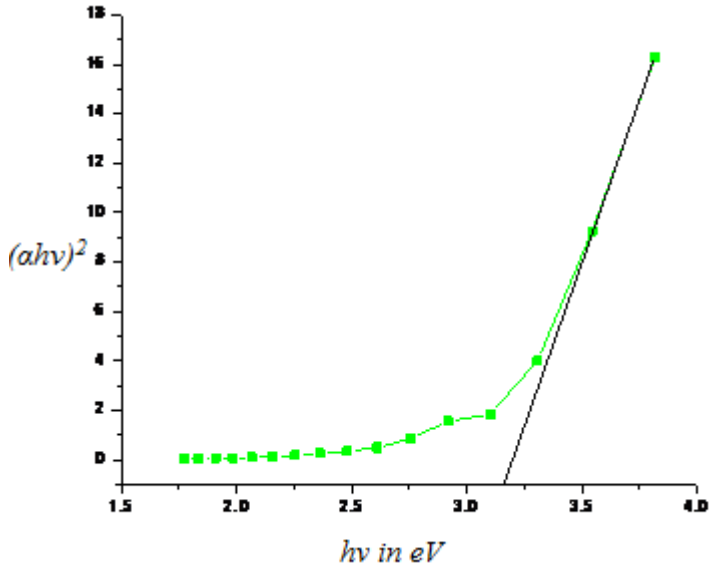

Figure 5. Energy band gap determination of ZnS thin film

CONCLUSION

ZnS nano thin film was effectively synthesized by CBD technique. The crystallite size of ZnS thin film calculated by Scherrer equation was 2nm.energy band gap calculated from optical studies was 3.16eV. Nano ZnS thin film was employed for the photocatalytic degradation of VB dye. The photocatalytic degradation was achieved upto 97.5% for 400mg/L dye concentration at pH 8. It indicates good applicability of nano ZnS thin films for environmental pollution control by removal of dyes from aqueous solution.

Acknowledgements
The authors have gratefully acknowledged to Central Instrumentation Centre, University Institute of Chemical Technology, NMU, Jalgaon for SEM and XRD analysis and Dr. Shirish Sonawane (NIT Warangal) for his valuable suggestions. Authors are also thankful to Principal, Kisan College, Parola and Principal, GTP College, Nandurbar for providing necessary laboratory facilities.

REFERENCES

[1] Gomaa OM, Linz JE, Reddy CA, *World J Microbiol Biotechnol*, **2008**, 24, 2349.
[2] Kumar M, Tamilarasan R, *J Mater Environ Sci*, **2014**, 5, 510.
[3] Rbas OD, Alkan M, An MD, *Adsorption*, **2002**, 8, 341.
[4] Patil SP, Shrivastava VS, Sonawane GH, *Desalin Water Treat*, **2015**, 54, 374.
[5] Mahmoodia NM, Arami M, Gharanjig K, *Desalin Water Treat*, **2009**, 1, 312.
[6] Boye B, Dieng MM, Brillas E, *Environ Sci Technol*, **2002**, 36, 3030.
[7] Marathe YV, Ramanna MMV, Shrivastava VS, *Desalin Water Treat*, **2013**, 51, 5813.
[8] Di Paola A, García-López E, Marcì G, Palmisano L, *J of Hazard Mater*, **2012**, 211-212, 3.
[9] Rajamanickam D, Shanthi M, *Toxico Env Chem*, **2013**, 95, 1484.
[10] Sahraei R, Aval G M, Goudarzi A, *J Alloys & Comp*, **2008**, 466, 488.
[11] Sahraei R, Motedayen Aval G, Baghizadeh A, Lamehi-Rachti M, Goudarzi A, Majles Ara MH, *Materials Letters*, **2008**, 62, 4345.
[12] Hwang DH, Ahn JH, Hui KN, Hui KS, Son YG, *Nanoscale Res Lett*, **2012**, 7, 26.
[13] Ates A, Yildirim MA, Kundak M¸ Yildirim M, *Chinese Journal of Physics*, **2007**, 45, 135.
[14] Kumar V, Saroja M, Venkatachalam M, Shankar S, *Int J Innovative Res in Sci Eng Tech*, **2014**, 3, 14875.
[15] Yadav AA, Barote MA, Masumdar EU, *Materials Chemistry and Physics.*, **2010**, 121, 53.