Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.769720

51 (2013) 5813–5820
August

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of nanocrystalline CdS thin films grown by chemical bath deposition at different molarities for removal of methylene blue

Yogesh V. Marathe[a], M.M.V. Ramanna[b], V.S. Shrivastava[a,*]

[a]*Nano-chemistry Research Laboratory, (Affi. to North Maharashtra University, Jalgaon), G.T.P. College, Nandurbar 425412, India*
Emails: gtpcollege@rediffmail.com, prorvinodshrivastava@gmail.com
[b]*Department of Chemistry, University of Mumbai, Kalina Campus, Santacruz (E), Mumbai, India*

Received 25 February 2012; Accepted 19 December 2012

ABSTRACT

In this work, chemical bath deposition technique has been used to prepare nanocrystalline CdS thin films on glass substrate at different molarities. The structural and morphological characterizations of nanocrystalline thin films were performed by X-ray diffraction and scanning electron microscopy techniques. The crystallite size found was in the range of 15–45 nm. The optical characterizations of thin films were performed using UV–visible spectroscopy. The optical band gap of chemical bath deposited thin films found to be in the ranged from of 2.30 to 2.45 eV. All thin films have high transparency, that is, greater than 60% in visible spectrum. Thin film prepared at different preparation condition was employed in photocatalytic oxidation of water soluble hazardous cationic methylene blue (MB) dye. Different parameters like the initial dye concentration, pH, and contact time have been studied and optimized. The results showed that MB was successfully removed from aqueous solution in photocatalytic system using thin films obtained at different molarities. The optimum conditions for degradation of dye were pH = 8.5, Initial concentration 30 mg/L and contact time 30 min. It was observed that increase in molarity decreases the grain sizes, which in turn increases the band gap and hence increase in photocatalytic efficiency of nanocrystalline CdS thin film.

Keywords: CdS; Chemical bath deposition (CBD); Thin film; Band gap; SEM; XRD; Photocatalytic; Methylene blue

1. Introduction

Ever increasing growth of industrialization and urbanization causes gigantic problem of environmental pollution. An industry consumes large quantity of water for their processes. The effluent coming out from textile and printing, pulp, and paper, sugar distillery etc are highly colored and contain highly toxic organic and inorganic contaminants and thereby causes environmental pollution which is the area of concern and there is need to pay attention on it. Due to industrial growth, the environmental pollution has

*Corresponding author.

been increased and it has attained a level high in developing countries. Cationic dyes are the largest group of the dyes used for dyeing cotton fabrics in the industry [1]. Methylene blue (MB), a cationic dye is the most commonly used substance for coloring among all the dyes of its category. MB can cause eye burns and if swallowed it causes irritation to the gastro intestinal tract with symptoms of nausea, vomiting and diarrhea. It may cause metheloglobinemia and dyspnea if inhaled [2]. Therefore, it is necessary to devise an effective method of waste water treatment in order to remove MB from textile effluent. The conventional biological treatment methods are ineffective for the complete color removal and degradation of organics and dyes [3,4]. In recent years, an alternative to conventional methods semiconductor photocatalysis is used to degrade organic pollutants in water to less harmful materials [5]. During the past two decades, photo-assisted catalytic degradation of organic pollutants in water and waste-water employing semiconductor as photocatalyst has been a promising technique [6–13]. Numerous studies have been carried out across the globe focusing on removal of dyes from textile water [6–10].

Recent studies have focused on the important photocatalytic applications of semiconducting material. The advance oxidation processes based on the chemical, photochemical and photocatalytic production of hydroxyl radical ($OH^{\bullet}$), which is acting as a strong oxidizing agent that has emerged as a promising technology for degradation of dyes. The conventional methods for waste water treatment includes coagulation filtration which are ineffective for the complete removal of contaminants as these methods can only transfer pollutants from one phase to another phase.

In heterogeneous photocatalysis, the solution of dye was exposed to light in presence of semiconductor, the MB molecule is excited to their first singlet state. These excited molecules are converted to their triplet excited state through inter system crossing. The CdS uses the light energy to excite its electron from valence band to conduction band thus leaving behind hole (h^+). Then h^+ subtract an electron from OH^- ion and generate $^{\bullet}OH$ radical which are strong oxidizing agent and can have ability to oxidize pollutant to different fragments which are less harmful, after successive free radical attack and fragmentation, most of organics mineralize to CO_2 and mineral acid [19].

The photocatalytic oxidation process is of huge importance for the effective removal of wide variety of organics [13]. Generally, two forms of CdS in photocatalysis have been used including a highly disperse fine particles or suspended particles in liquid medium and thin film on solid support [14]. When suspension of CdS particles applied in photocatalysis system, the suspended CdS particle needs to be separated upon completion of each reaction cycle. However, this problem could be avoided by using CdS thin films.

The preparation of thin film of CdS is one of the major researches in photocatalytic field. In order to identify the optimum conditions for deposition, it is necessary to study various conditions during deposition of thin film. Extensive research has been carried out in the field of semiconducting material thin film for their immense use in thin film photocatalysis for pollution control. These films have gain enormous importance in research for their potential environmental application due to low cost and energy efficient. There are many techniques reported to fabricate CdS chalcogenide thin films such as spray pyrolysis [15], close space sublimation [16], physical vapor deposition [17], electrodeposition, magnetron sputtering [18]. All these methods have sophisticated requirement in terms of high vacuum, precise temperature control and high cost of equipment. However, the chemical bath deposition (CBD) technique [19] is the best suited technique for the thin film deposition because of its simplicity, convenience, least expense to produce uniform adherent and reproducible large area thin films. Also this method allows achieving good CIGS. CdS diodes in solar cells [20,21]. In the present communication, results on synthesis and systematic optical characterization [22] and photocatalytic application of nanocrystalline CdS thin film at different molar concentration of cadmium have been reported.

2. Experimental

2.1. Materials and method

Analytical grade reagents were used without further purification for the preparation of CdS thin films. $CdBr_2$ and thiourea was used as precursor solutions. The water-soluble MB dye M.F. $C_{16}H_{18}N_3SCl$ (Fig. 1), and nanocrystalline CdS thin films were used for active oxidation process. The stock solution of 50 mg/L of MB was prepared in 100 mL deionized water. In 20 mL of dye solution three film catalysts (1×2.5 cm^2)

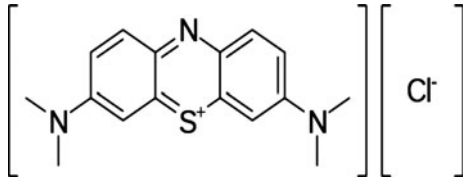

Fig. 1. Structure of MB.

were immerged. Then, solutions were irradiated in close box with an UV lamp which emits light having $\lambda = 254$ nm and intensity of 37.4 mW/cm^2. The reaction rate was followed by taking out sample after regular interval and analyzed then by an UV–visible double-beam spectrophotometer at $\lambda_{max} = 664$ nm.

2.2. Thin film preparation

In present work, the nanocrystalline CdS thin films have been synthesized by CBD technique. The deposition was carried out by using aqueous solution of cadmium bromide (Aldrich 98%) and thiourea which were chosen as a main precursor of Cd and S, respectively. For the preparation of CdS, thin films at three different concentration of cadmium bromide (0.04, 0.08, 0.12 M) have been used. After complete dissolution of cadmium bromide, the pH of the solution was maintained at >9 by adding slowly ammonia solution then equimolar solution (Cadmium bromide solution) of thiourea was added to the cadmium bromide solution and the temperature of the solution was maintained at 85˚C. The commercial soda lime glasses were used as a substrate which were cleaned several times by detergent and then boiled in chromic acid (2 M) for 30 and thoroughly washed in deionized water, then very clean glass substrate was mounted vertically in solution for 90 min. After the complete formation of film, the substrate were removed from the bath and rinse with warm deionized and then film again ultrasonically cleaned in deionized water using ultrasonic water bath (6.5 L 200, Systronics, India Ltd, Mumbai) and dried in air. The X-ray difractogram were recorded by using Philips PW-3710 X-ray defractometer with Cu Kα at room temperature. The morphological studies of the thin films were done by using scanning electron microscopy (SEM). Optical absorbance and transmittance spectra of all thin films were recorded using UV–visible double-beam spectrophotometer (Systronics 2203) in the spectral range 350–850 nm. The obtained nanocrystalline thin films then employed for photocatalytic experiments.

2.3. Photocatalytic experiment

2.3.1. Instrumentation

The photocatalytic degradation of MB dye was carried out in a photocatalytic reactor, which consists of a cylindrical Pyrex glass rector, a double-walled quartz cooling water jacket and 400 W medium pressure Hg lamp with nominal wavelength range 220–1,400 nm. The cooling water jacket was set up inside the reactor to maintain the temperature to be within range of 25–31˚C, hence preventing excessive heating of the reaction mixture. The reaction solution was stirred with magnetic stirrer at a constant speed to maintain well mixed during the experiment. The pH measurements were made on equiptronics a digital pH meter (Model-E610) fitted with glass electrode which was previously standardized with buffer of known pH. The change of dye concentration was measured by spectrophotometrically.

3. Result and discussion

3.1. XRD studies

In general, CdS exists in two crystal structures cubic and hexagonal. It has been reported that chemical bath deposited or chemically deposited CdS films depending upon preparative conditions, show cubic, hexagonal or mixed (cubic + hexagonal) crystal structures. CBD-CdS crystals show three diffraction peaks at 27θ, 43θ, and 52.5θ which are associated with the (002), (110) and (112) reflections of the hexagonal modification or (111), (220) and (331) reflections of the cubic CdS structure [14]. It is mentionable that the identification and assignments of the observed diffraction patterns were made using the JCPDS data and by comparison with published results [23].

The XRD (Philips PW-3710 X-ray defractometer) studies of CdS thin film prepared at different molar concentration are shown in Fig. 2. It is observed that XRD pattern shows preferred orientation along (002) plane. The grain size calculated by using Scherer formula [23] is shown in Table 1.

$$D = k\lambda/\beta\cos\theta$$

where D is grain size, k is a constant taken to be 0.94, B is the full width at half maximum and λ is wavelength of X-ray. Due to size effect, the peaks in the diffraction pattern broaden and their widths become larger as the particles become smaller. It was observed that crystallite size decreases with increase in molarity.

3.2. SEM analysis

SEM is a convenient technique to study of morphology of thin film. The SEM micrographs shown in Fig. 3 shows the surface morphology of the CdS thin film prepared for three different molarities. The micrographs shows that the films are not uniform throughout the entire region, but the films are without any void, pinhole or cracks. It is clearly observed from SEM micrograph that there is formation of nano-sized

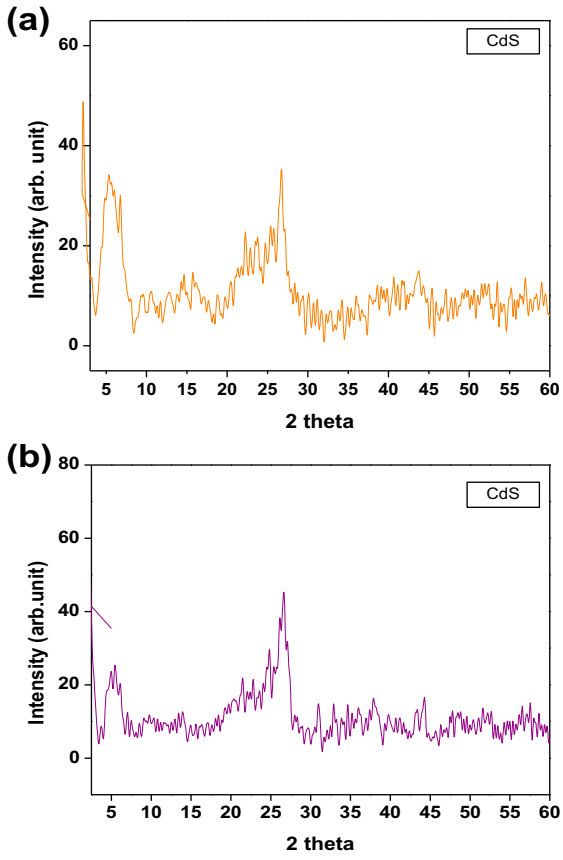

Fig. 2. XRD pattern of CdS nanocrystalline films at different molarities ($a = 0.04$ M, $b = 0.12$ M).

Table 1
The crystalline sizes and band gaps for nanocrystalline CdS thin films

Film No.	Molarity	Grain size(nm) from XRD	Band gap (eV) from UV
1	0.04 M	45	2.30
2	0.12 M	15	2.42

grains which gives evidence for the nanocrystalline nature of thin film. SEM micrographs also shows that grain sizes of thin film is not uniform, therefore average grain size were estimated and found in the range 103–264 nm.

3.3. Optical studies

The optical transmittance spectra of thin films are shown in Fig. 4. All the films shows high transmittance of more than 60% at wavelength longer than 500 nm and it keeps on increasing with wavelength.

The optical absorbance spectra of CdS thin films are shown in Fig. 5, from the spectrograph the absorption edge of sample found to occur in the range of 350–450 nm. The optical band gap E_g can be estimated from the tauc plot [24].

$$\alpha h_\upsilon = A(h_\nu - E_g)^n$$

where E_g is the band gap corresponding to particular transition occurring in film, A is a constant, υ is the transition frequency and the exponent n characterizes the nature of band transition. The plot between h_υ vs. $(\alpha h_\upsilon)^2$ is shown in Fig. 6. The extrapolation of straight line to $(\alpha h_\upsilon)^2 = 0$ axis gives the value of energy band gap of CdS thin film. The band gap of thin films observed in the range of 2.30–2.45 eV. It is observed that band gap increases with decrease in grain size.

3.4. Photocatalytic behavior

The photocatalytic removal of MB was studied at λ_{max} 664 nm. The optimum conditions for the removal of dye are 30 mg/L, pH 8.5 and contact time 30 min. The results obtained during this study are being presented in Figs. 7–9.

3.4.1. Effect of Initial dye concentration

The rate of photocatalytic degradation of MB by CdS thin films was studied by varying the dye concentration from 60 to 10 mg/L (Fig. 7) at fixed catalyst concentration active sites remain the same, the number of substrate ions accommodating the interlayer space increases so that the degradation decreases. Increase in the number of substrate ions accommodating in inter layer spacing inhibits the action of catalyst which thereby decreases the reactive (–OH) and free radicals attacking the dye molecule [25]. Also as the concentration of dye increases the color of solution becomes more intense and it alters the light to reach the dye molecule and thereby decreases the degradation efficiency of catalyst.

It was clearly observed in Fig. 7 that removal percent of thin film prepared at 0.12 M is higher at optimum concentration 30 mg/L than other two thin films.

3.4.2. Effect of pH

The pH of the aqueous solution is an important operational parameter in the process. The effect of pH on photocatalytic degradation was also investigated. The results are reported in Fig. 8. It is evident from the data that the rate of photocatalytic bleaching of dye increases with increase in pH. The increase in the

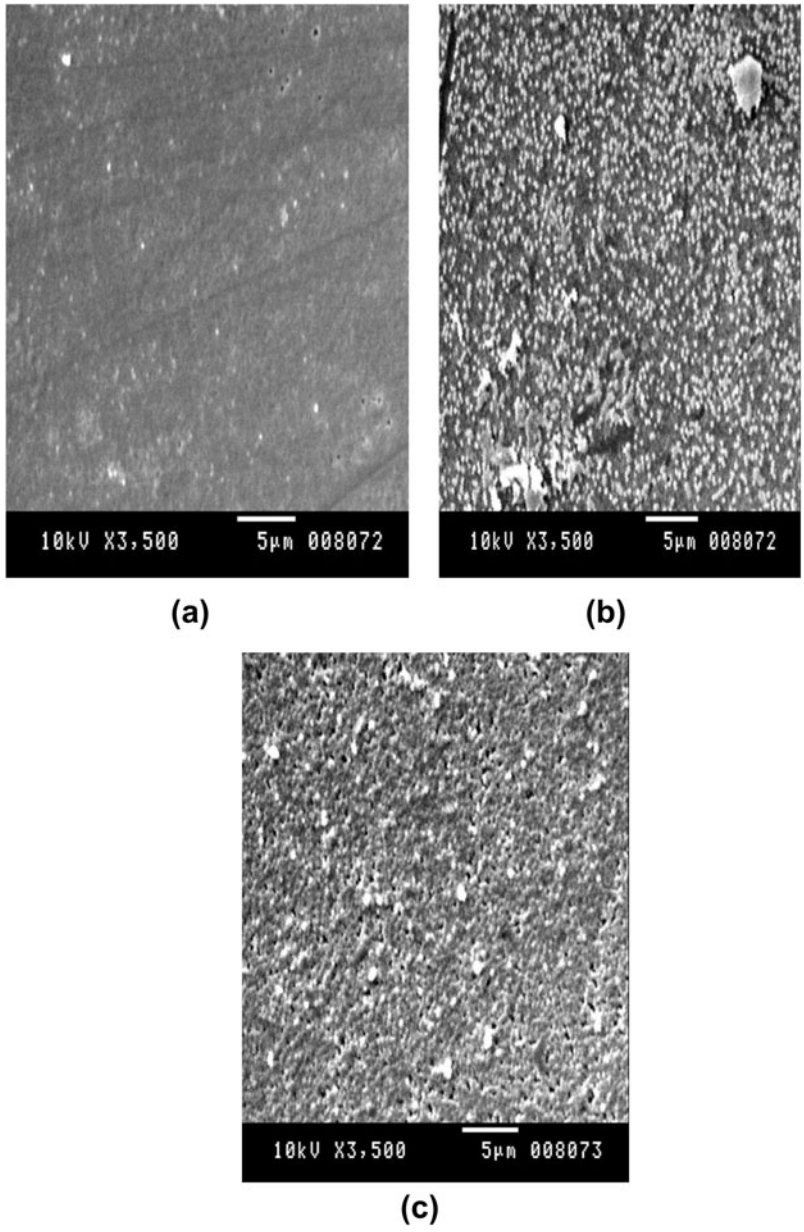

Fig. 3. SEM micrograph of CdS nanocrystalline films for different molarities ($a = 0.04$ M, $b = 0.08$ M, $c = 0.12$ M).

rate of photocatalytic bleaching may be due to the availability of dye in its anionic form, which is attracted towards positively charged surface of the semiconductor. The effect of pH may be explained on the basis of efficient generation of hydroxyl radical by CdS, with increase in concentration of hydroxide ions. It is apparent that the rate of degradation of MB with increase in pH value up to 8, this may be due to the fact that as the pH increases onwards 8, the repulsion of the dye anion by negatively charged CdS surface would results in the reduction in efficiency of degradation of MB. The removal percent of MB at different pH by three different thin films shows variation in percent removal. Thin film deposited at 0.12 M showed effective removal than other two thin films.

3.4.3. *Effect of contact time*

The effect of contact time for removal of MB by nanocrystalline CdS thin films deposited at different molar concentration is shown in Fig. 9. There was rapid removal of dye observed in the first 30 min. and then removal rate decreased gradually and reach to equilibrium in about 50 min.

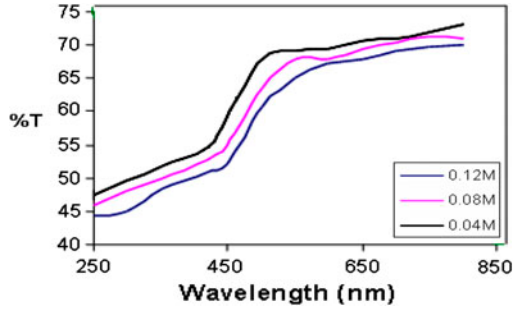

Fig. 4. Transmittance spectra of CdS nanocrystalline films at different molarities.

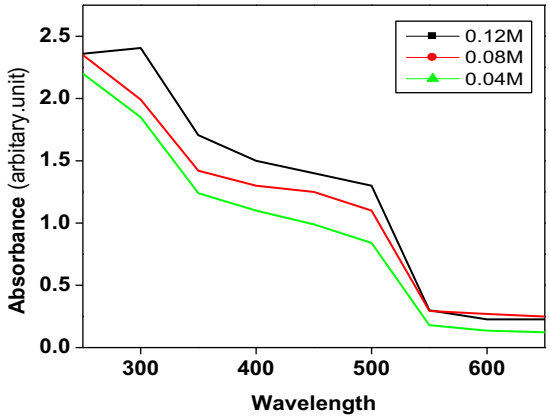

Fig. 5. UV-absorption spectra of CdS nanocrystalline films at different molarities.

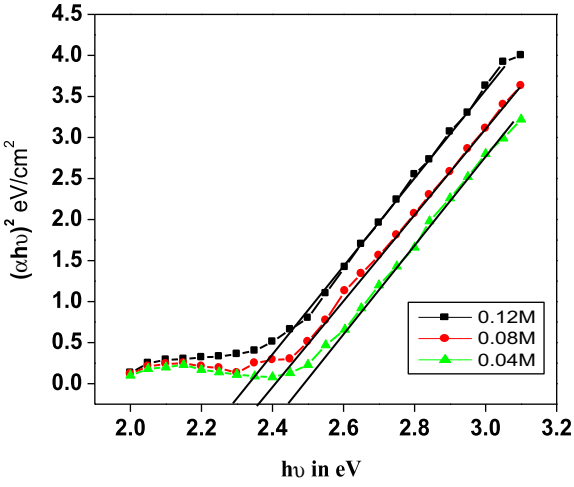

Fig. 6. Energy band gap determination of CdS thin films at different molarities from h_υ vs. $(\alpha\ h_\upsilon)^2$.

At the beginning, removal rate was fast as the dye was adsorbed by the exterior surface of the CdS. Thin film deposited at molar concentration 0.12 M shows greater photocatalytic behavior than deposited at 0.4 and 0.8 M concentration.

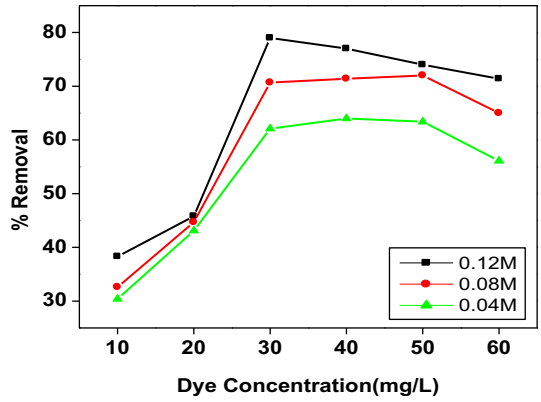

Fig. 7. Effect of initial dye concentration on percentage removal of MB dye by using thin films prepared at different molarities.

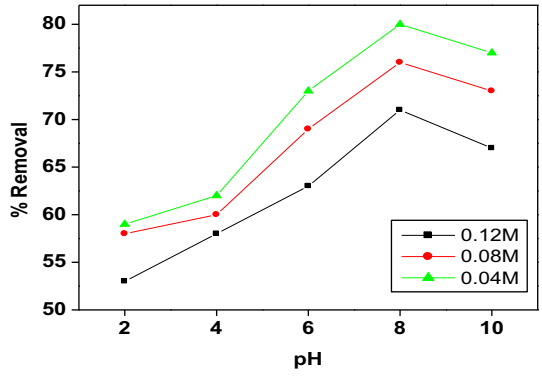

Fig. 8. Effect of pH on percentage removal of MB dye at 30 mg/L concentration by using thin films prepared at different molarities.

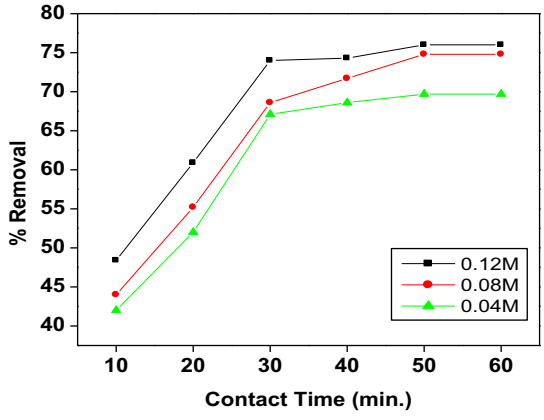

Fig. 9. Effect of contact time on percentage removal of MB dye at 30 mg/L concentration and pH 8.5 by using thin films prepared at different molarities.

3.5. Kinetic study

On the basis of thin film photoactivity studies further investigations were conducted to understand

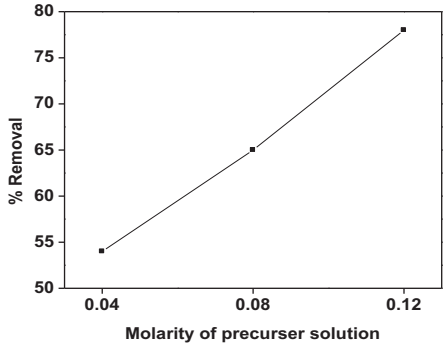

Fig. 10. Photocatalytic activity of nanocrystalline CdS thin film derived at different molarities.

Table 2
The reaction rate constant for MB photocatalytic removal using thin films prepared at different molarities and at pH = 8.5, Initial concentration 30 mg/L and contact time 30 min

Sample no.	Molarity	k (min^{-1})
1	0.04	0.0651
2	0.0.8	0.0891
3	0.12	0.097

effect of different thin film preparation conditions on photocatalytic performance. Fig. 10 shows the effect of concentration of precursor solutions on thin film deposition and their effects on its photocatalytic activity.

The reaction rates statistically found to follow first-order kinetic model of which reaction rate constants were determined by statistically fitting with experimental data and results to be 0.0651, 0.0891 and 0.097 min^{-1} for thin films obtained at different concentration of precursor solutions 0.4, 0.8 and 0.12, respectively. These results indicate that the photocatalytic activity of nanocrystalline thin film prepared at 0.12 M concentration was highest among all three thin films tested. Fig. 10 shows the effect of concentration of precursor solutions in nanocrystalline CdS thin film preparation on the photocatalytic process. The reaction rate constant of each thin film are also presented in (Table 2). It was found that CdS thin film deposited at 0.12 M concentration exhibited higher photocatalytic activity in MB removal with a value of reaction rate 0.097 min^{-1}. This may be explain on the basis of characterization results which shows that as molarity of precursor solution increases the crystallite size of CdS in thin film decreases. Also as size decreases the surface area available increases subsequently % removal of MB increase, also as concentration of precursor solutions increases the band gap also increase, therefore as a result of increase in band gap electron hole pair recombination rate decreses in CdS hence rate of photocatalytic degradation of MB increases. However, application of thin films prepared at 0.4 and 0.8 M concentration shows less photocatalytic efficiency than film prepared at 0.12 M concentration this may be due to increase in grain size and small band gap (for film prepared at concentration 0.04 and 0.08 M).

These results substantiate that the photocatalytic process is considerably affected by thin film preparation conditions. Hence, photocatalytic property can be related to crystallite size and band gap of CdS thin film.

4. Conclusion

It is possible to synthesize the nanocrystalline CdS thin film through CBD technique. The XRD study confirms the formation of nano-sized crystals in thin film. The crystallite size was within range of 15–45 nm. The optical studies of thin films performed by UV–visible spectroscopy clearly showed an increase in band gap with molarity which supports the formation of nano-sized grains in CdS thin film. Band gap calculated were in the range of 2.32, 2.37, and 2.45 eV. It was also revealed that band gap increases with a decrease in grain size. The photocatalytic experiments show that the properties of CdS thin films are considerably influenced by their preparation conditions. The photocatalytic activity of obtained thin films for the degradation of MB was studied. It was found that differences in photocatalytic oxidation of MB could be correlated with the grain size and band gap of CdS in thin film. Thin film obtained at 0.12 M concentration provides high efficiency in MB removal due to the small grain size and large band gap of thin film material. The overall deposition method and photocatalytic experiment clearly showed that higher molarity facilitates the growth of nano-sized crystals and increase in band gap in CdS thin film and this results in increased photocatalytic property of CdS thin film which is good environmental pollution control applications.

Acknowledgment

Authors are greatfully acknowledged to the UGC-New Delhi for financial support by the grant no.F-38-67/2009 (SR) dated 19/12/2009. Authors are also thankful to the IIT, Mumbai and Head of Department of Physics, North Maharashtra University, Jalgaon for SEM and XRD studies.

References

[1] V.S. Shrivastava, The biosorption of Safranine onto *Parthenium hysterophorus* L: Equilibrium and kinetics investigation, Desalin. Water Treat. 22 (2010) 146–155.

[2] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Biosorption of Acid Blue 15 using fresh water macroalga Azolla filiculoides: Batch and column studies, Dyes Pigm. 71 (2006) 77–82.
[3] R.H. Souther, T.A. Alspaugh, Textile wastes recovery and treatment sewage and industrial wastes, J. Water Pollut. Control Fed. 29 (1957) 918–934.
[4] A. Hamaran, M. F. Hamoda, Proceedings of the 35th waste congress, Lafaytte, IN, 1980.
[5] F.B. Li, X.Z. Li, K.W. Cheah, Photocatalytic activity of neodymium ion doped TiO_2 for 2-mercaptobenzothiazole degradation under visible light irradiation, Environ. Chem. 2(2) (2005) 130–137.
[6] D.F. Ollis, C.S. Turchi, Heterogenous photocatalysis for water purification: Contaminants mineralization kinetics and elementary reactor analysis, Environ. Prog. 94 (1990) 229–234.
[7] D.W. Pohanmann, Mechanisms on organic transforms on semiconductor particles, In: E. Pellezzetti, M. Schiavello (Eds.), Photochemical Conversion and Storage of Solar Energy, Kuwer Academic, Dordrecht, 1991 pp. 251–276.
[8] A. Mills, S.L. Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A 108 (1997) 1–35.
[9] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. National Renewal Energy Laboratory, Golden, CO, 1999. pp. 35–98.
[10] M.I. Litter, Heterogenous photocatalysis transition metal ions in photocatalytic systems, Appl. Catal. B 23 (1999) 89–114.
[11] J.M. Hermann, Heterogenous photocatalysis: Fundamentals and application to the removal of various types of aqueous pollutants, Catal. Today 53 (1999) 115–129.
[12] N.M. Mahmoodia, M. Arami, K. Gharanjig, Laboratory studies and CFD modeling of photocatalytic degradationof colored textile wastewater by titania nanoparticles, Desalin. Water Treat. 1 (2009) 312–317.
[13] B. Boye, M.M. Dieng, E. Brillas, The catalytic degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, Environ. Sci. Technol. 36 (2002) 3030–3035.
[14] X. Yin, G. Xin, F. Zhang, S. Wang, G. Zhang, Kinetic study on photocatalytic degradation of 4BS azo dye over TiO_2 in slurry, Environ. Eng. Sci. 23 (2000) 1000–1008.
[15] D. Kaji, C. Sanjiviraja, Ramachandran Thermal and structural properties of spray pyrolysed CdS thin film, Bull. Mater. Sci. 28 (2005) 233–238.
[16] T.L. Chu, S.S. Chu, High efficiency thin film CdS/CdTe solar cells, Int. J. Sol. Energy 12 (1992) 121–132.
[17] R.W. Birkmire, B.E. Mccandless, S. S Hegedes, Effects of processing on CdTe/CdS materials and devices, Int. J. Solar Energy 13 (1992) 145–154.
[18] J. Pouzet, J.C. Bernede, A. Kelil, H. Essaidis, Benhida Preparation and characterization of tungsten diselenide thin films, Thin Solid Films 208 (1992) 252–259.
[19] J.H. Lee, J.S. Yi, K.J. Yang, J.H. Park, R. Oh, Electrical and optical properties of boron doped CdS thin films prepared by chemical bath deposition, Thin Solid Films 431–432 (2003) 344–348.
[20] K. Ramanathan, M.A. Contreras, C.L. Perkins, S. Asher, F.S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Nou, J. Ward, A. Duda, Properties of 19.2% Zno/CdS/CulnGaSe2 thin film solar cells, Prog. Photovoltaics 11 (2003) 225–230.
[21] H. El Maliki, J.C. Bernede, S. Marsillac, J. Pinel, X. Castel, J. Pouzet, Study of the influence of annealing on the properties of CBD-CdS thin films, Appl. Surf. Sci. 205 (2003) 65–79.
[22] A.E. Rakhshani, Study of Urbach tail, bandgap energy and grain-boundary characteristics in CdS by modulated photocurrent spectroscopy, J. Phys. Condems. Matter 12 (2000) 4391–4400.
[23] P. Scherrer, Gothinger Nachri-Chten Gesell 2 (1918) 98.
[24] X.L. Tong, D.S. Jiang, W.B. Hu, Z.M. Liu, M.Z. Luo, The comparison between CdS thin films grown on Si(111) substrate and quartz substrate by femtosecond pulsed laser deposition, Appl. Phys. A 84 (2006) 143–148.
[25] P.N. Gibson, M.E.O. Zsan, D. Lincot, P. Cowache, D. Summa, Modeling of the structure of the thin films, Thin Solid Films 361 (2000) 34–40.