

Photodegradation of Rhodamine-B under natural sunlight using CdS_xSe_{1-x} chalcogenides

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Abstract: The present work represents the synthesis of CdS_xSe_{1-x} Nano crystallites by wet chemical precipitation method using dichloroacetic acid as a complexing agent. The prepared CdS_xSe_{1-x} Nano crystallites is characterized by XRD and SEM for their structural and morphological studies. The formation mechanisms of the material were investigated and discussed on the basis of the experimental results. Photodegradation of Rhodamine-B dye from water is carried out under natural sunlight using prepared CdS_xSe_{1-x} Nano crystallites and investigated under UV-Vis-NIR spectrophotometer and FT-IR methods.

Key words: Nano crystallites, Chalcogenides, X-ray Diffraction, Photodegradation.

1. INTRODUCTION

The ternary semiconducting compounds have received the more attraction of many researchers due to the considerable properties. It is found that, it shows uses in optoelectronic devices. It shows considerable band gap energy. The chalcogenide semiconductors have several important applications in the modern technology and industry, where they can be used in electronics, opto-electric, microelectronics, communication, catalysis, coating and energy generation progress (Yu et al, 2004). Chalcogenide materials like CdS_xSe_{1-x} have good electrical properties as well as the optical band gaps can be tuned by means of changing the composition of the elements. Therefore, CdS_xSe_{1-x} Nano crystallites have many applications and are used in several optical devices (Apte et al, 2006). In previous studies, Khomane(2013), Hassanien et al(2016) estimated structural and optical properties of ternary CdS_xSe_{1-x} chalcogenides. It can be used in photodegradation of organic pollutants. Rhodamine –B dye is one of the major pollutants found in textile and dye industries. In present work we have prepared Ternary CdS_xSe_{1-x} crystallites with wet chemical precipitation method in aqueous medium using dichloroacetic acid is a complexing agent with uniform growth rate for fast release of Cd^{2+} ion. This prepared material is characterized and analyzed for photodegradation of organic water pollutant like Rhodamine-B dye.

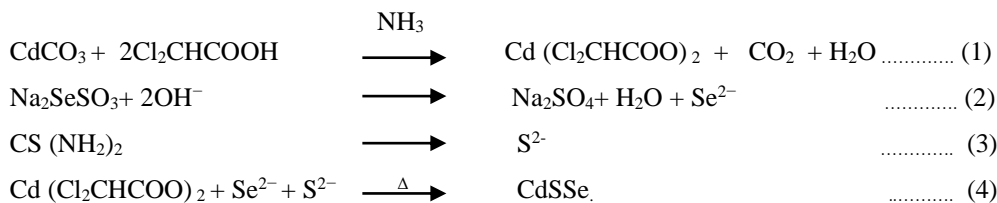
2. MATERIALS AND METHODS

2.1 Preparation of CdS_xSe_{1-x} Nano crystallites

The CdS_xSe_{1-x} material was obtained by wet chemical precipitation method at temperature $80 \pm 5^\circ C$ and pH-10. Chemicals used for preparation of CdS_xSe_{1-x} were SD fine analytical grade cadmium carbonate, selenium black powder, sodium sulfite, thiourea, dichloroacetic acid, ammonia and de-ionized water. The solution of 0.2M sodium selenosulfate (Na_2SeSO_3) prepared by 12g of sodium sulfite in 200 ml water was refluxed with 5g of selenium for almost 10 hr. at $80 \pm 5^\circ C$.

The solution of 0.2 M cadmium dichloroacetate was prepared by dissolving cadmium carbonate ($CdCO_3$) in equivalent solution of 0.2M dichloroacetic acid ($pK_a=1.35$ at $25^\circ C$) with constant stirring. The dichloroacetic acid forms complex with Cd^{2+} ions and gives cadmium dichloroacetate solution. The aqueous NH_3 was added from a burette in reaction mixture to maintain the basic condition (pH=10) of the solution. Equimolar solution of 0.2 M sodium selenosulfate dissolved in de-ionized water was added used as a source of Se^{2-} ions and 0.2M Thiourea was added as a source of S^{2-} ion. This reaction mixture was kept in a water bath and the temperature of the water bath was optimized to $80 \pm 5^\circ C$. (Khomane, 2013). The cadmium dichloroacetate has two electronegative Cl^- groups which fascinates the release of Cd^{2+} ions from complex under optimized temperature conditions. The electronegative Cl^- group increases the rate of reaction due to inductive effect on substrate moiety and one can get CdS_xSe_{1-x} after 90 minutes. The prepared CdS_xSe_{1-x} was annealed at $200^\circ C$ for 2hr and introduced for characterization.

2.2 Growth Mechanism



3. RESULT AND DISCUSSION

3.1 X-ray diffraction study of CdS_xSe_{1-x}

The prepared CdS_xSe_{1-x} material was analyzed for crystallographic identification by JEOL X-ray diffractometer (Model JSDX-60PA) with Cu Kα1-radiation source has wavelength λ = 1.54184 Å. XRD-spectrum of CdS_xSe_{1-x} shown in Fig.1. The analysis showed that the prominent reflections are observed due to the (002), (101), (102), (110), (200) and (203) planes of hexagonal crystal structure as compared with standard JCPDS data (00-049-1459).

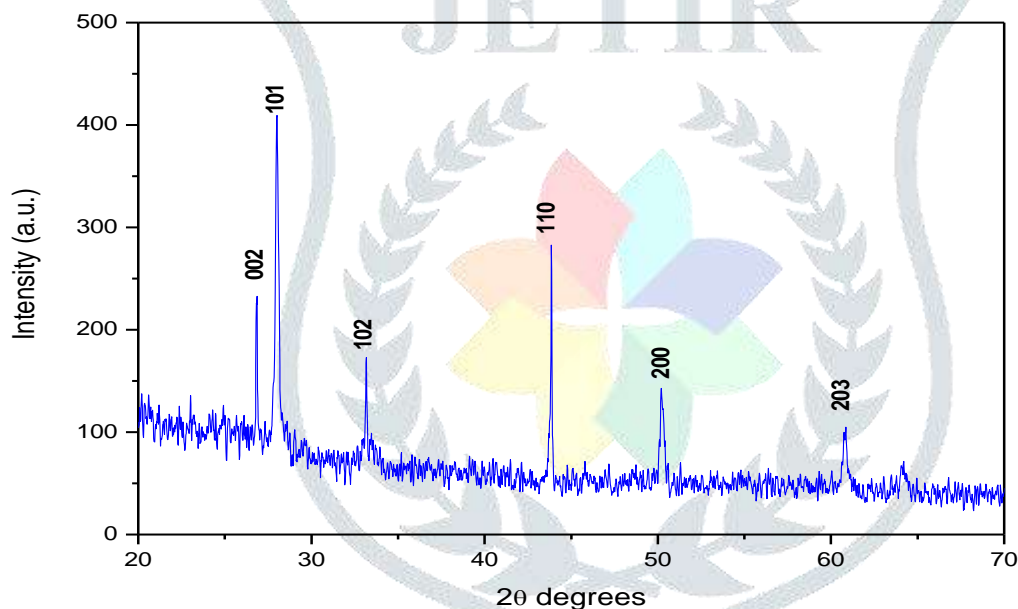


Figure1. X-ray diffraction spectrum of CdS_xSe_{1-x}

The lattice parameters have been calculated by using the following equations.

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \dots\dots\dots (5)$$

Where ‘d’ is the inter-planar distance and(hkl) are Miller indices of the lattice planes. The lattice parameters ‘a’ and ‘c’ of hexagonal CdS_xSe_{1-x} phase were found to be in the order of 4.1885 Å and 6.6570 Å respectively shown in Table.1. The grain size (D) has been calculated by using Scherrer's formula.

$$D = K\lambda / \beta \cos\theta \dots\dots\dots (6)$$

Where K is constant (0.94), λ = 1.54184 Å is the wavelength of the X-ray used, β is broadening of diffraction line measured at half of its maximum intensity (in radian) and θ is Bragg's diffraction angle. The observed grain size for CdS_xSe_{1-x} is 58.6 nm shown in Table.1. (ChenMing-Liang et al, 2011, Rabinovich et al, 2013, Zhou Ru et al, 2016).

Table1. Structural parameter and grain size of CdS_xSe_{1-x}

| Sample | 2θ Values | | hkl planes | d-values A° | Cell parameter A° | Grain size (nm) |
|--------|-----------|----------|------------|-------------|--------------------------------|-----------------|
| | Standard | Observed | | | | |
| CdSSe | 26.27 | 26.80 | 002 | 3.3286 | a= 4.1885 and c = 6.6570 | 58.6 |
| | 27.99 | 28.02 | 101 | 3.1856 | | |
| | 36.34 | 33.12 | 102 | 2.7059 | | |
| | 43.29 | 43.88 | 110 | 2.0634 | | |
| | 50.38 | 50.20 | 200 | 1.8177 | | |
| | 62.50 | 60.85 | 203 | 1.5226 | | |

3.2 Surface morphological analysis of CdS_xSe_{1-x}

The powdered CdS_xSe_{1-x} Nano crystallites were analyzed using Cambridge Stereo Scan (USA) Scanning Electron Microscope for surface morphological analysis (Murray et al, 1993, Robel et al, 2006, Kumara et al, 2012). The analysis was carried out at 2 μm magnification. The SEM analysis shows that ternary CdS_xSe_{1-x} having crystalline nature. The grains of prepared CdS_xSe_{1-x} material have irregular shapes as shown in Fig.2.

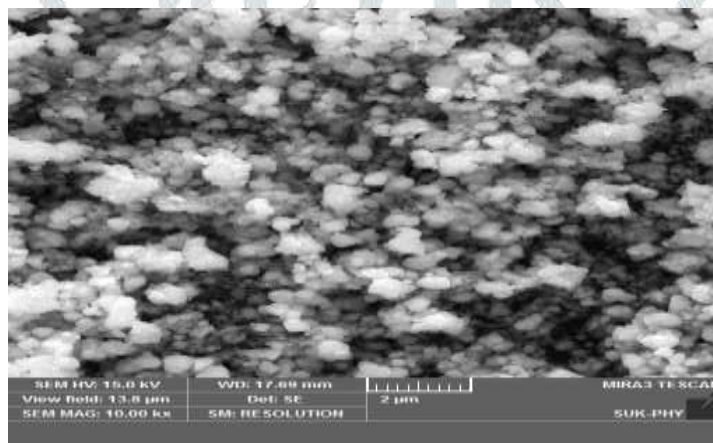


Figure2. SEM image of CdS_xSe_{1-x}

3.3 Photodegradation of Rhodamine-B

The photodegradation of Rhodamine-B dye is carried out under natural sunlight in day time using prepared CdS_xSe_{1-x} Nano crystallites. The test performed at neutral pH, 100mg of CdS_xSe_{1-x} material was added to 100 mL of 10ppm Rhodamine-B solution in 250ml clean and dry borosil glass beaker. Before irradiation to sunlight, the solution mixed with material was sonicated for 15min then it was kept in the dark for at least 1 hr. allowing the adsorption/desorption equilibrium to be reached. Then, the solution was irradiated with sunlight with constant stirring. The first sample was taken before the irradiation in order to determine the Rhodamine-B concentration in solution after dark adsorption, which was after considered as the initial concentration (A_{initial}). Samples were then withdrawn regularly from the beaker by an order of 30, 60, and 90minutes irradiated and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-vis-NIR spectrophotometer at wavelength range from 400 to 800nm and the value of 90min was taken (A_{final}). The efficiency of photodegradation of Rhodamine-B dye by CdS_xSe_{1-x} material in presence of natural sunlight was estimated at 90 minutes. (Hemmateenejad et al,2015, Barkul et al, 2017, Licheng Huang et al, 2018, Kayode et al, 2019). The efficiency of material was calculated by using following equation.

$$\text{Efficiency}(\%) = \frac{[A_{\text{initial}} - A_{\text{final}}]}{A_{\text{initial}}} \times 100 \dots \dots \dots (7)$$

It was observed that prepared CdS_xSe_{1-x} material has about 90% efficiency for degradation of Rhodamine-B which is enhanced photocatalytic property of prepared material for degradation of organic dye in natural water shown in Fig.3.

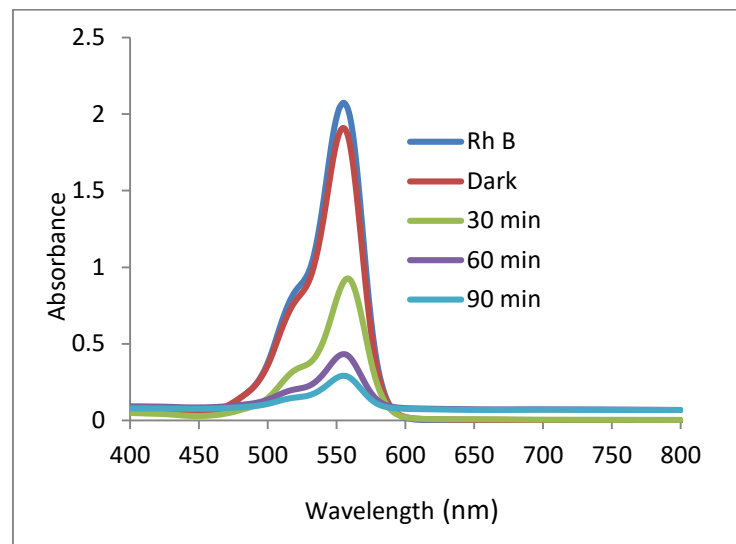


Figure3. UV-Vis-NIR spectrum for photodegradation of Rhodamine-B

3.3 FT-IR study of Rhodamine-B dye

The photodegradation of Rhodamine –B dye was also measured on Fourier Transform Infrared Spectroscopy analysis technique (Bruker). The transmittance of Rhodamine-B dye was measured against wave number and is shown in the Fig.4. The Rhodamine-B dye shows peaks at 1584.04 cm^{-1} and 1407.21 cm^{-1} are due to aromatic C-C vibrations. The peak observed at 1338.43 cm^{-1} is due to carbon-aryl bond vibrations and peak at 1175 cm^{-1} is due to presence of alkyl chloride group. The peaks observed at 1067.48 and 1004.92 are due to the asymmetric stretching of carbon-oxygen-carbon bond. The peak observed at 680.71 due to the bending vibrations of aromatic ring. The solution of Rhodamine-B with $\text{CdS}_x\text{Se}_{1-x}$ after 90minutes were analyzed under FT-IR shows vanishing of majority of peaks of Rhodamine-B confirms degradation of dye shown in spectrum.

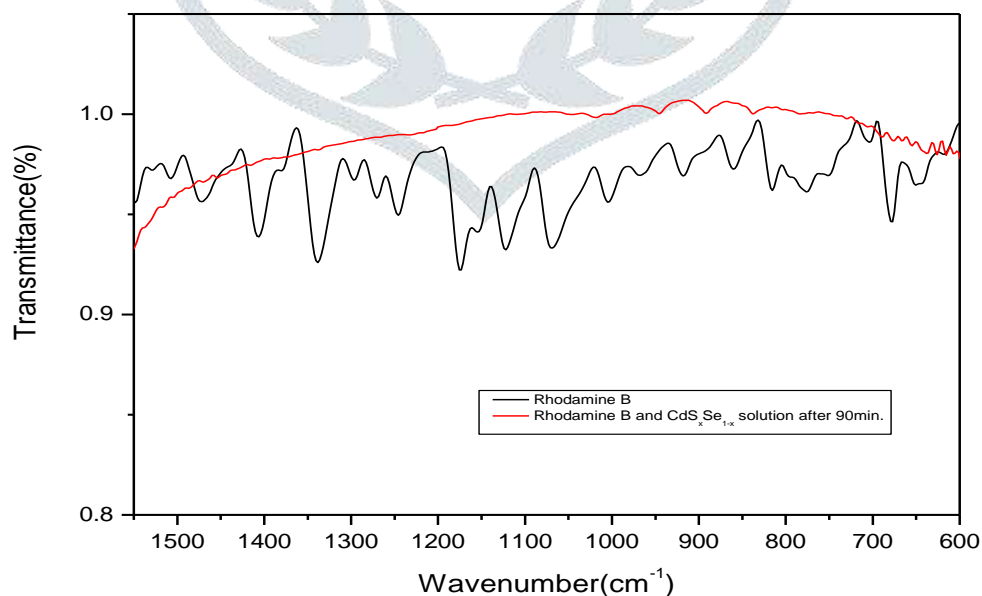


Figure4. FT-IR spectrum of Rhodamine-B

4. CONCLUSION

The CdS_xSe_{1-x} Nano crystallites were synthesized by wet chemical precipitation technique using dichloroacetic acid as a complexing agent have hexagonal phase. The dichloroacetic acid fascinates easy release of Cd²⁺ in solution due to inductive effect of electronegative Cl⁻ ions. The lattice parameters 'a' and 'c' of hexagonal CdS_xSe_{1-x} phase were found to be in the order of 4.1885 Å and 6.6570 Å respectively. The prepared CdS_xSe_{1-x} material shows grain size of 58.6 nm and it can be efficiently used for degradation of Rhodamine-B dye or for similar types of organic pollutants in natural water.

REFERENCES

- [1] Yu W.W, Qu L, Guo W, Peng X. 2004. Experimental determination of the extinction coefficient of CdTe, CdSe and CdS Nanocrystals. *Chem. Mater*, 16:560-568.
- [2] Apte S.K, Kale B.B, Sonawane R.S, Naik S.D, Bodhale S.S, Das B.K. 2006. Homogeneous growth of CdS/CdSSe nanoparticles in glass matrix. *Materials Letters*, 60:499-503.
- [3] Khomane A.S. 2013. Crystallographic and microscopic properties of ternary CdS_{0.5}Se_{0.5} thin films. *Optik*, 124:2432-2435.
- [4] Hassanien A.S, AklAlaa A. 2016. Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. *Superlattices and Microstructures*, 89:153-169.
- [5] ChenMing-Liang, OhWon-Chun. 2011. Synthesis and highly visible-induced photo catalytic activity of CNT-CdSe composite for methylene blue solution. *Nano scale Research Letters*. 6:398-405.
- [6] Rabinovich E., Hodes G. 2013. Effective Band gap Lowering of CdS Deposited by Successive Ionic Layer Adsorption and Reaction. *J. Phys. Chem. C*, 117:1611-1620.
- [7] Zhou Ru, Wan Lei, NiuHai hong, Yang Lin, Mao Xiaoli, Zhang Oifeng, Miao Shiding, Xu Jinzhang, Cao Guozhong. 2016. Tailoring band structure of ternary CdS_xSe_{1-x} quantum dots for highly efficient sensitized solar cells. *Solar Energy Materials and Solar Cells*, 15:520-529.
- [8] Murray C.B, Norris D.J, Bawendi M.G. 1993. Synthesis and characterization of nearly monodisperse CdE (E = sulfur selenium, tellurium) semiconductor nanocrystallites. *J. Am. Chem. Soc.*, 115:8706–8715.
- [9] Robel I, Subramanian V, Kuno M, Kamat P.V. 2006. Quantum Dot Solar Cells Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO₂ Films. *J. Am. Chem. Soc.*, 128:2385–2393.
- [10] KumaraVipin, Dwivedi DK. 2012. Study on structural, optical and electrical properties of CdS_{0.5}Se_{0.5} thin films for photovoltaic applications. *Optik*, 124:2345-2348.
- [11] Hemmateenejad Bahram, Shadabipour Parisa, Tahereh Khosousi, Shamsipur.2015. Chemometrics investigation of the light-free degradation of methyl green and malachite green by starch-coated CdSe quantum dots. *J Industrial and Engineering Chemistry*, 27:384-390.
- [12] Barkul Rani P, Patil Meghshyam K, Patil Satish M, Shevale Vrushali B, Delekar Sagar D. 2017. Sulight-assisted photocatalytic degradation of textile effluent and Rhodamine B by using iodine doped TiO₂ nanoparticles. *Journal of photochemistry and photobiology A: Chemistry*, 349:138-147.
- [13] Licheng Huang, Wencheng Fang, Ying Yang, Jie Wu, Hui Yu, Xiangting Dong, Tingting Wang. 2018. Three dimensional MoO₃ Nanoflowers assembled with nanosheet for Rhodamine B degradation under visible light. *Materials Research Bulletin*, 108:38-45.
- [14] Kayode Adesina Adegoke, Muzaffar Iqbal, Louis Hitler, Olugbenga Solomon Bello. 2019. Synthesis characterization and application of CdS/ZnO nanorod heterostructure for the photodegradation of Rhodamine-B dye. *Material Science for energy technologies*, 2:329-336.