

INTERCALATION OF CdS INTO LDH LAYERED HOST FOR DEGRADATION OF RHODAMINE –B AND ANTIBACTERIAL ACTIVITY

K. KARTHIKEYAN^{ab*}, A. THIRUMOORTHY^c

^aResearch and Development centre, Bharathiar University, Coimbatore, Tamilnadu, India

^bPresent address: Guest Lecturer, Department of chemistry, Government Arts College, Udumalpet, 642 126, Tamilnadu, India

^cAssistant Professor, Post Graduate Department of Chemistry, Government Arts College, Udumalpet – 642 126, Tamilnadu, India.

Layered double hydroxides (LDHs) intercalated CdS nano composites has been synthesized and photo catalytic activity of the products has been studied by a photo catalytic degradation of Rhodamine B in aqueous solution under visible light irradiation. SEM pictures revealed that agglomerated CdS formed in the layered host. Photoluminescence (PL) studies show the band gap 2.47eV. The electron-hole recombination enhanced photo catalytic activity of LDH-CdS. The XRD confirms intercalation by improves interlayer distance of LDH about 0.029nm and also LDHs- CdS using for antibacterial agent.

(Received July 13, 2016; Accepted September 16, 2016)

Keywords: Cadmium sulphide, LDH, Intercalation, Nano composites, Anti bacterial agents, Staphylococcus aureus

1. Introduction

Cadmium Sulfide (CdS) compound semiconductor using wide range of potential applications. It has existed in cubic or hexagonal forms and wide- direct-band gap semiconductors. The CdS is used with the semiconductor cadmium telluride to fabricate solar cells given which gives band gap energy (2.42eV) for optical windows, while great importance in the optoelectronic applications and a diverse range of applications. The semiconductor including as waveguides, hetero junction devices and in thin-film electroluminescent displays in which it is the most commonly used host material. In CdS used in solar cells and the use of wider band gap materials such as ZnS or CdZnS could lead to decreases in window absorption losses and improvements in the short circuit current of the cells [1, 5].

Layered double hydroxides (LDHs) structured like are the host guest layered material consisting of positively charged metal hydroxide layers acting as host. LDHs can be expressed by a formula, $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/n}^{n-}.m\text{H}_2\text{O}]$ where M^{2+} and M^{3+} represent divalent and trivalent metal cations within the layers, and A^{n-} is the interlayer anion, such as CO_3^{2-} , ClO_4^- , Cl^- , and NO_3^- etc. Synthesis and chemical modification of LDHs posses attractive research opportunities such as catalysis, medicinal materials, waste removal, polymer nano composite, and drug delivery have already been reported [6-11].

*Corresponding author: kathiravanbinthu@gmail.com

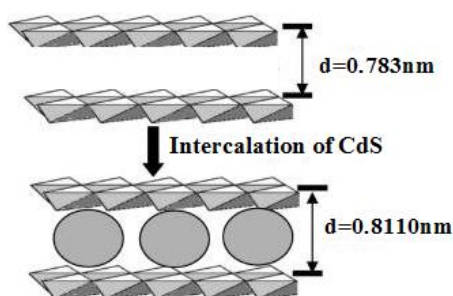


Fig.1 Schematic representation of the LDH structure before and after CdS intercalation

Herein, we report our recent efforts on synthesis of the LDHs-intercalated CdS nanoparticles (LDHs-CdS) through ion-exchanging process. The visible light photo catalytic activity investigated for degradation of Rhodamine B (RhB). It was found that the LDHs-CdS possesses better visible light photo catalytic activity than LDHs. The respectable band gap energy arises for LDHs-CdS than LDHs. In addition, intercalation effects in XRD analysis confirmed intercalation of CdS in layered host of LDHs. The PL studies shows doublet broad peak for LDHs-CdS for sulphur vacancies. The photo catalytic activity of RhB- dye degradation has been calculated by dye removing percentage for various interval times. Anti bacterial studies was investigated by film contact method for 12.5, 25, 50 μg of LDHs-CdS Nano composites against *Staphylococcus aureus*.

2. Experimental Section

2.1 Preparation of LDHs

A co-precipitation method was employed under controlled pH conditions, prepare Ni/ Fe-LDHs with a molar ratio of $\text{Ni}^{2+}/\text{Fe}^{3+} = 3:1$. The samples were synthesized by adding 1.5 mol Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mol Fe $(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into 30 ml deionized water under vigorous stirring at room temperature. The final pH of the reaction mixture was adjusted to 10.0 with ammonium carbonate solution. The resultant mixture was refluxed at 65 $^\circ\text{C}$ for 1 h. After that brown coloured solid was filtered and washed with distilled water to remove excess free ions until the pH of the filtrate was 7. The washed precipitate was dried at 60 $^\circ\text{C}$ overnight, and used for CdS intercalation.

2.2 Preparation of Intercalated LDHs-CdS

1 g of LDH in 100ml aqueous solution containing 0.5 gm of Na_2S flakes stirring for 5 Hrs then filtered and washed to remove excess of sulphides ions then 0.1 mole of Cd^{2+} ions were added stirring then washed and dried 60 $^\circ\text{C}$ for LDH-CdS formation.¹⁴ (interionic exchange method).

3. Result and Discussion

The intercalation was elaborated by XRD which shows Ni^{2+} - Fe^{3+} LDHs and CdS intercalated LDHs shown in Fig 2. The precursor, Ni^{2+} - Fe^{3+} LDHs has a basal spacing of 0.783 nm and no peaks of impurities are obtained which indicating a high purity of the product (Fig. 1a). The precursor form could be converted to CdS intercalated LDHs material inter layered spaces was increased from 0.783 to 0.8110 nm¹² since CdS has been intercalated in the layer spaces of LDH. In XRD pattern shows the 002 crystalline plane of the CdS shifted to $2\theta = 30.0477$ since Ni and Fe ions present in LDH.¹³

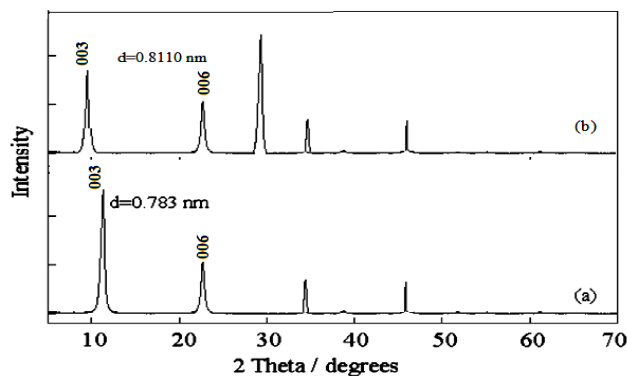


Fig.2 X-ray powder diffraction pattern of (a) LDHs (b) LDHs-CdS

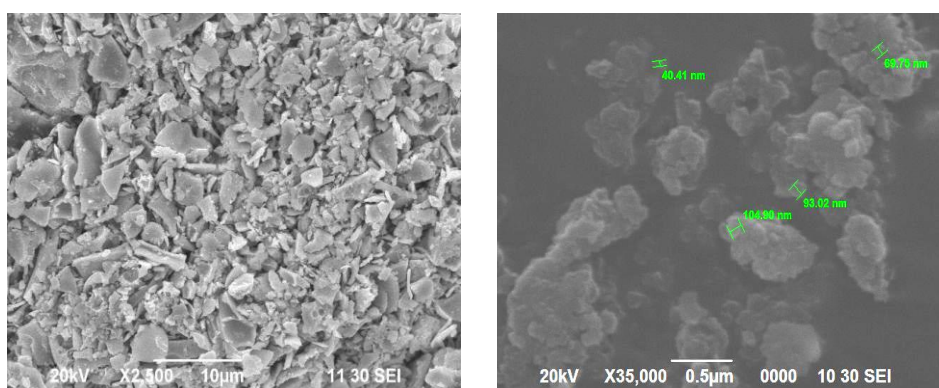


Fig.3 SEM image of (a) LDHs (b) LDHs-CdS nano composites

The morphology of the Ni- Fe LDHs material was characterized by scanning electron microscope (SEM). In figure 3(a) plate-like and a number of hexagonal shape morphology was observed¹⁴. In figure 3(b) shows the intercalated CdS nano composites agglomerated grains are not uniform. Consequently the grain sizes found to be 67 to 73 nm.

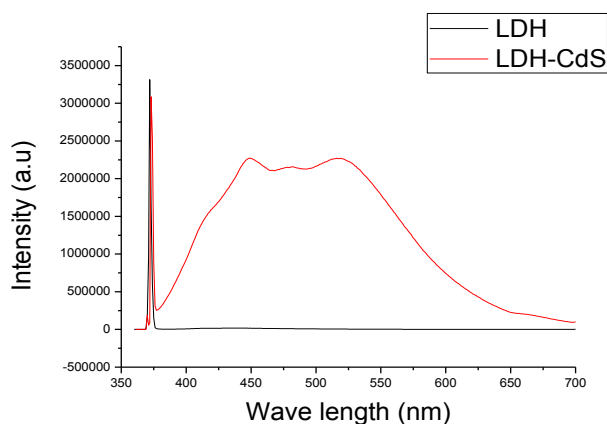


Fig.4 PL spectra of LDHs and LDHs-CdS

Optical property of LDHs-CdS was investigated by Photoluminescence spectra. In Fig.4 shows the broad doublet peak at 400 to 625nm for LDHs-CdS which elaborated that CdS present with dopants. In this case CdS doublet peak range 620-850nm¹⁵ has been shifted to lower (blue

shift) for LDHs-CdS since CdS present in the layered host of the LDH which forms new kind of sulphur vacancy also stronger attraction with electrons or holes and forms band gap 2.47eV. Meanwhile LDHs was not shows any peaks.

FT-IR spectra of synthesized LDHs were shown in figure 5. In figure 5(a) the LDHs exhibits strong absorption due to the interlayer nitrate at 1361.79 cm^{-1} , while after the intercalation, the nitrate absorption has gone down in intensity and absorption due to intercalated CdS nano particles and the lattice vibration modes as M-O-H at 655.82 cm^{-1} . In figure 5 (b) shows the absence of peak around 1360 cm^{-1} since CdS intercalation took place which gives the 632 cm^{-1} for CdS-stretching¹⁶⁻¹⁸

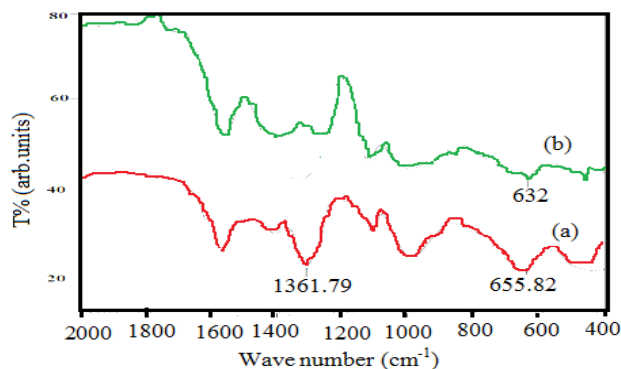


Fig.5 FT-IR spectra of (a) LDHs (b) LDHs-CdS

Dye removal

Fig. 6 shows that kinetic of dye removal percentage of Rhodamine-B by photo catalytic reaction on LDHs- CdS. The 100 ml of RhB solution with a concentration 50 mg l^{-1} was involved in adsorption with 10 mg of nano particles. The mixture was stirred at room temperature and samples of the reaction mixture were withdrawn at desired time intervals ranging from 10 to 30 min during the adsorption process. Effect of adsorption time on Rh-B removal by LDHs- CdS was examined at different time interval and Eq. (1) was used to calculate the colour removal efficiency.

$$R\% = \left[\frac{C_0 - C}{C_0} \times 100 \right] \quad (1)$$

C_0 and C were the initial and present concentrations of the dye in solution (mg/l), respectively. It was found that the Rh-B removal percent increased with increasing contact time. The UV-visible spectra indicates for LDHs- CdS was low dye adsorption rate during the first 10 min and a higher uptake rate thereafter. Above the 20 and 30 min dye adsorption increased and reach 83% which calculated by eq1. LDHs involve in dye adsorption through the interlayer distance where adsorption process high initially then lower. In CdS intercalated LDH shows the adsorption took high percentage after 10 min as cadmium sulphide nano particles present in inter layered LDHs sheet and induces photo catalytic activity.

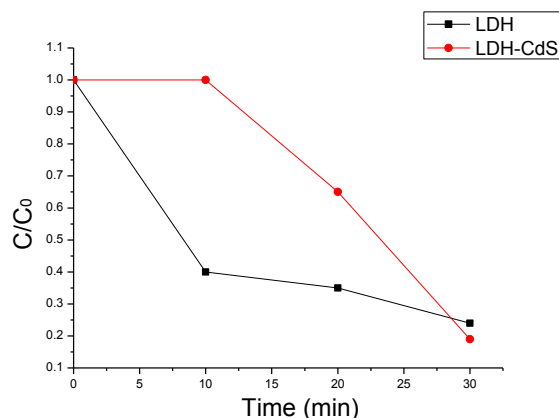


Fig.6 Kinetics of the degradation of LDHs-CdS.

Antibacterial studies

Fig.7 Shows that anti bacterial activity of synthesized LDHs-CdS nano composites were performed for *Staphylococcus aureus* by film contact method for 30min using 12.5, 25 and 50 μg of LDHs-CdS nano composites. These various ration of nano particles antibacterial activity has been investigated which found 30%, 55% and 67%. The anti bacterial activity increases with composite ratio which effective against bacteria and greater damage for the function of *Staphylococcus aureus*.



Fig.7 Anti bacterial activity of LDHs-CdS against *Staphylococcus aureus*.

4. Conclusions

In summary, LDHs-CdS were obtained via inter ionic removing method. The interlayer distance confirmed that intercalation of semiconductor nano particles. The samples showed band gap as electron hole recombination sulphur with Ni and Fe ions and enhanced photo catalytic activity under visible light irradiation. The percentage of dye removal of LDHs shows enhanced initially since dye intercalated after decreased which confirmed that those are not involved in photo catalytic activity. In LDHs-CdS dye removal occurs through photo catalytic degradation which confirms dye removal percentages. LDHs-CdS has better antibacterial agents against *Staphylococcus aureus*.

Reference

- [1] R. B. Kale, C. D. Lokhande, Appl. Surf. Sci. **252**, 929 (2005).
- [2] H. Tang, Mi Yan, Hui Zhang, M Xia, DerenYang, Materials letter **59**, 1024 (2005).
- [3] Pankaj Tyagi, A G Wedeshwar, Bull. Mater. Sci. **24**, 297 (2001).
- [4] S Shrivastava, Verma B Cryst. Res. Technol. **42**, 466 .

- [5] J Barman, J P Borah, K C Sarma, Chalcogenide Letters **5**, 11 (2008).
- [6] F Bergaya, B K G Theng and G Lagaly, Handbook of Clay Science, Developments in Clay Science, Vol. 1, Chapter 13.1 (2006).
- [7] E Geraud, V Prevot, C Forano and Mousty, C Chem. Commun. 1554 , (2008).
- [8] M B J Roeffaer, B F Sels, H Uji-i, F C DeSchryver , P A Jacobs, D E De Vos, J Hofkens, Nature **439**, 572 (2006).
- [9] J Das, B S Patra, N Baliarsingh and K M Parida ,Appl. Clay Sci. **32**, 252 (2006).
- [10] F Zhang, L Zhao, H Chen, S Xu, D G Evans and Duan X. Angew, Chem. Int. Ed. **47**, 2466 (2008).
- [11] K M Tyner, S R Schiffman and E P J Giannelis, Controlled Release **95**, 501 (2004).
- [12] J H Lee, S W Rhee, D Y Jung, Chem. Mater. **16**, 3774 (2004).
- [13] S S Kavar and B H Pawar, Chalcogenide Letters **6**, 219 (2009) .
- [14] Chanchal Chakraborty, Kausik Dana and Sudip Malik , J. Phys. Chem. C **115**, 1996 (2011)
- [15] Fuyi Chen and Wanqi Jie, Cryst. Res. Technol. **42**, 1082 (2007).
- [16] T P Martin Spectrochim. Acta A **38**, 655 (1982).
- [17] R He Mater. Lett. **57**, 1351 (2003).
- [18] D H Williams and Fleming, Spectroscopic methods in organic chemistry (NewDelhi, Tata McGraw-Hill) p. 57 (2004).