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Synthesis of nanocrystalline CdS from Cd (II) complex of S-methyl dithiocarbazate ligand as a single source precursor

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Abstract :

In the Present Work, we have reported the single X-ray crystal structure of the cadmium (II) S-methyl dithiocarbazate (SMDTC) complex [Cd $(SMDTC)_2$] Cl_2. The compound has been found to be an effective single source precursor for the preparation of CdS NCs via microwave assisted method. The possible mechanism for the anisotropic growth of cadmium sulfide-NCs is also discussed with its characterization by ir, u.v-visible, photoluminescence, X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) spectroscopy.

Key words : Cds, microwave, precursor, photoluminescence.

INTRODUCTION:-

Recently, one of the most important endeavour for scientists and engineers worldwide is developing a sustainable and renewable future[1,2]. Among various II-VI semiconductor materials, cadmium sulphide (CdS) has been extensively investigated and used as an important direct-bond semiconductor, photoelectric conversion in solar cell, light-emitting diodes for flat-panel display and other optical devices based on its nonlinear properties[3-5]. The reported single source precursors are the organo-metallic complexes of relatively small molecular weight chelates like chalcogenates[6], thio/selenocarboxylate[7,8], xanthates[9], thiourea[10,11], dithiocarbamate[12,13], dithiophosphinates[14] and dithiocarbazates[15] Firstly, it produced mterials with uniform dimensions of high purity due to low thermal gradient in the medium. Secondly, it possesses high reaction rates,

because microwave rate of nucleation and reduces the synthesis time[16].

In this paper, we reported a simple microwave irradiation method for the synthesis of CdS rod-shaped nanoparticles through dithiocarbazate ligand as a single molecular precursor source. The obtained CdS nanoparticles are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transition electron microscopy (TEM), U.V.-Visible and FTIR spectroscopy. The effect of irradiation time on the size and degree of crystallinity and optical band of CdS nanoparticles are investigated.

EXPERIMENTAL :

Materials used :

Analytical grade chemicals and reagents; potassium hydroxide (KOH), hydrazine hydrate, carbon disulfide, ethanol, methyl iodide, 3,5-dibromo-4-hydroxy benzaldehyde and cadmium acetate metal salt of Sigma- Aldrich are used throughout the work.

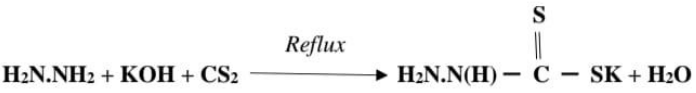
Instruments used: Electrical stirrer, water bath, ultra sonication microwave oven.

Precursor synthesis :

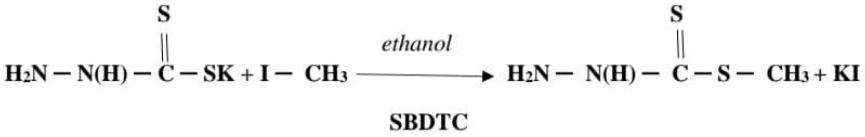
The synthesis of SMDTC is carried out as previously [1]. 11.4g (0.2 moles) of KOH dissolved in (9:1) 70 ml absolute ethanol and then 10g (0.2 mole) of hydrazine hydrate ($NH_2.NH_2.H_2O$) is added in the cooled upto $0^{\circ}C$ above solution slowly with constant stirring and the mixture is cooled to $0^{\circ}C$ in ice bath. Another solution of CS_2 15.2g (0.2 mole) prepared by adding in 12.5 ml ethanol is added dropwise via a dropping funnel to the above mixture, while the mixture is still being kept in the ice bath. Now vigorous mixing is performed via a mechanical stirrer. After constant stirring for one hours, the two layers formed in which lower yellow oily layer is separated using a separating funnel, and was then dissolved in 12ml of cold 40% absolute ethanol maintain at 5-7$^{\circ}C$. The mixture is kept in an ice bath again and 10ml CH_3I is added slowly in the mixture with vigorous stirring for 30 minutes more. The milky mixture formed is then filtered and washed with water and finally left to dry over silica gel.

Yield : 50%

M.P : 82$^{\circ}C$



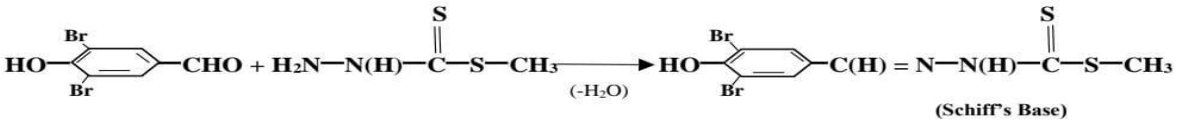
(Reaction-1)



(Reaction-2)

Synthesis of Schiff base :

The novel Schiff base is prepared by the simple condensation reaction between 3,5-dibromo-4-hydroxy benzaldehyde and S-methyldithiocarbazate.



(Reaction-3)

Synthesis of transition metal complexes :

The Schiff base (0.002 mole) is dissolved in hot acetone (23ml). This was added to a solution of cadmium acetate (0.002 mole) in acetone (13ml) in 2:1 molar ratio. The resultant solution becomes coloured. The mixture was heated on water bath and refluxed upto an hour. When crystals of metal complexes started appearing, then refluxing was stopped and the reaction mixture was allowed to stand overnight where upon coloured crystals were formed. Precipitate was filtered off and the complex was purified in vacuum oven and dried with anhydrous $CaCl_2$ in a desiccator.

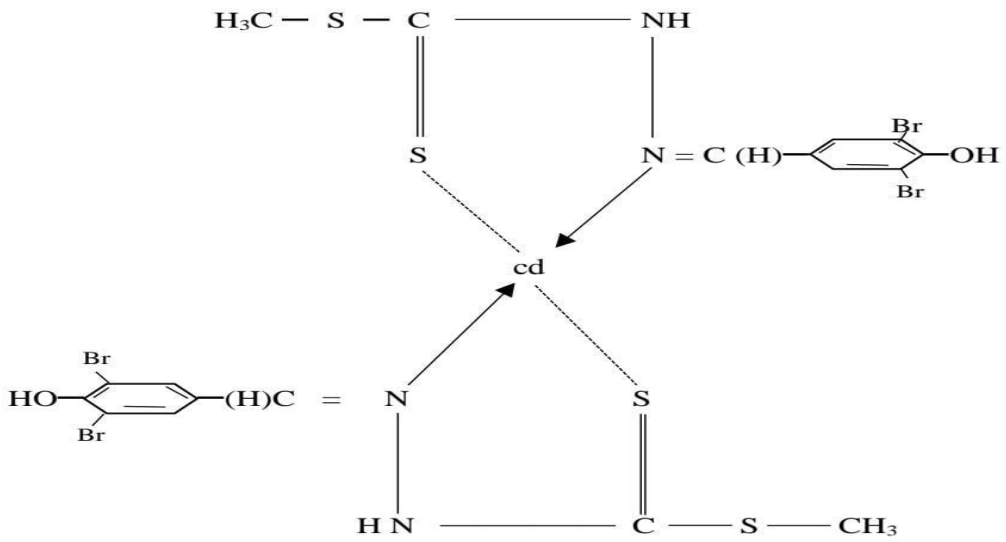


Fig.-1 : Sturcture of metal complex

Metal Complex : Bis-[S-methyl-β-N-(3,5-dibromo-4-hydroxy benzylidene) dithiocarbazate] cadmium (II).

Preparation of CdS-nanoparticles :

One (1.0 g) gm of cadmium complex was dissolved in 20 ml DMSO in a round bottom flask. A ultrasonic treatment was given to the solution for 30 minutes. For ultrasonic environment the mixture is immersed into an ultrasonic bath heated at 75℃ for 6 hours. Ultrasonic vibrations were generated by piezoelectric sandwich transducer at 40 KHz resonant frequency. The solution taken in the beaker was placed at the centre of the microwave oven and was irradiated with 90% power (800w) for scheduled time. Heating it for 10 minutes with 800w power microwave resulted spontaneous formation of CdS nanoparticles. The solution was cooled and washed with absolute methanol and chloroform. Precipitate was centrifuged and dried in air. Nanoparticles were collected and thoroughly washed with water and ethanol.

Characterization :

Nanocrystals were collected and their structural, morphological, and optical characterization is done by different instruments. Powder X-ray diffraction pattern is obtained from using X Pert Pro PAN analytical X-ray diffractometer in the 2θ ranging from 20^0 to $80^{\circ}C$ with CuKα radiation of wavelength 1.54 A^o. Elemental analysis is carried out from Carlo ERBA Model EA 1108 analyzer. Fourier infrared (FT-IR) spectra is recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. TEM and HRTEM were obtained by TECHAIG2F20 operated at 300KV using a drop of suspension of the sample in ethanol on carbon coated copper grid. Optical spectra of the CdS structures on quartz in the range 200-900 nm are obtained by Perkin Elmer Iambda 25 spectrophometer. Photoluminescence (PL) spectrum is obtained using Perkin Elmer PL-55 with exciton at 300 nm.

Results and discussions :

Green yellow coloured CdS nanoparticles were attained within a short reaction times using microwave heating in DMSO. Microwave irradiated materials are of high quality as microwave irradiation provides selective uniform heating, high reaction rate and low-energy consumption. The DMSO solvent also plays a very important role in nanorod synthesis. DMSO having high boiling point and high permanent dipole moment, is an excellent absorber of the microwave irradiation, which can take up the energy from the microwave field and get the polar reaction heated up to high temperature instantaneously. The polar solvent acting as both reaction media and dispersion media can efficiently absorb and stabilize the surface of the particles and produce monodispersed CdS nanoparticles[17]. The short reaction time results in increasing product purities by reducing unwanted side reactions. Microwave reactors allow easy access to high temperature and pressures. Structural, morphological and optical studies were performed on the samples.

Structural studies :

X-ray diffraction for CdS nanoparticle obtained (figure-2) by cadmium complex of 3,5-dibromo-4-hydroxy benzaldehyde Schiff's base of SMDTC shows its hexagonal structure. Reflections of the peaks are small and broad indicating small size of the particle. All observed peaks are matched with (100), (002), (101), (110), (103), (112), (004),(203),and (211). Formation of hexagonal phase exploit due to rapid formation of CdS nanostructure by microwave heating. The crystallite size of CdS is calculated by using Debye Scherrer formula $D = 0.9 \lambda / \beta \cos \theta$

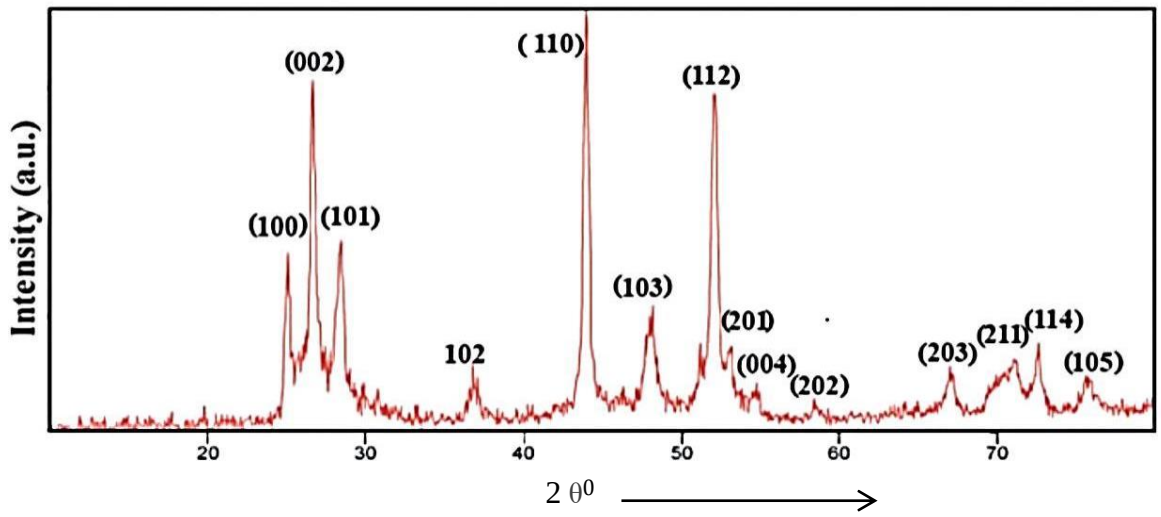


Fig.-2 : XRD-pattern of CdS Nanoparticles.

Morphological studies :

The morphology of CdS-NPs is examined by scanning electron microscopy (SEM) analysis (figure-3). Size of CdS-NPs as examined by SEM satisfies the values obtained by TEM analysis (figure-4). Long rod-shape particles are formed. Thickness of rods is about 75 nm with length more than 4-5μm Linear lattice plane are observed. Inter planar spacing is calculated and found to be equal to 0.35 nm. The presence of dark and bright fringes confirms the good crystalline structure.

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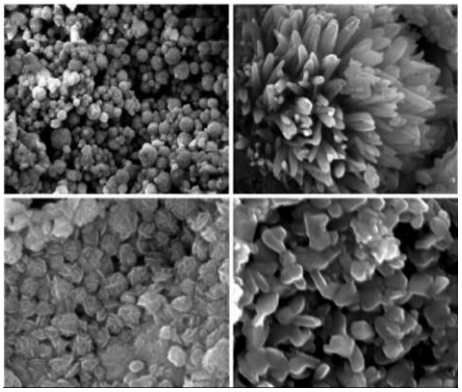


Fig.-3 : SEM images of CdS-NPs

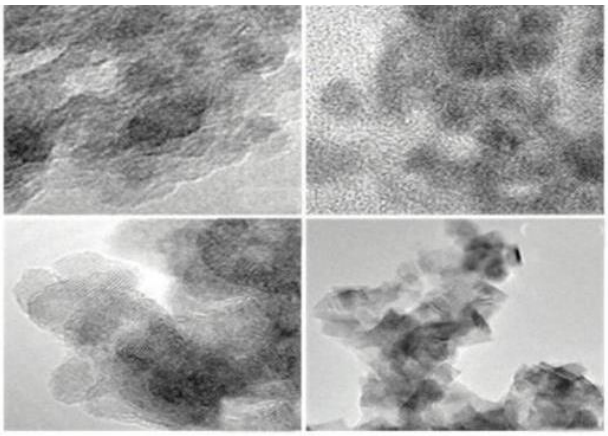


Fig.-4 : TEM images of Cds-NPs

Optical studies :

The optical absorption spectrum and emission fluorescence spectrum of a hexane solution containing nano-dispersed CdS are shown in Fig.-5. The optical absorption reduces to a few nanometers. The absorption maximum is clearly blue shifted to 460 nm, as compared to the bulk band gap of hexagonal CdS (490 nm, 252eV).

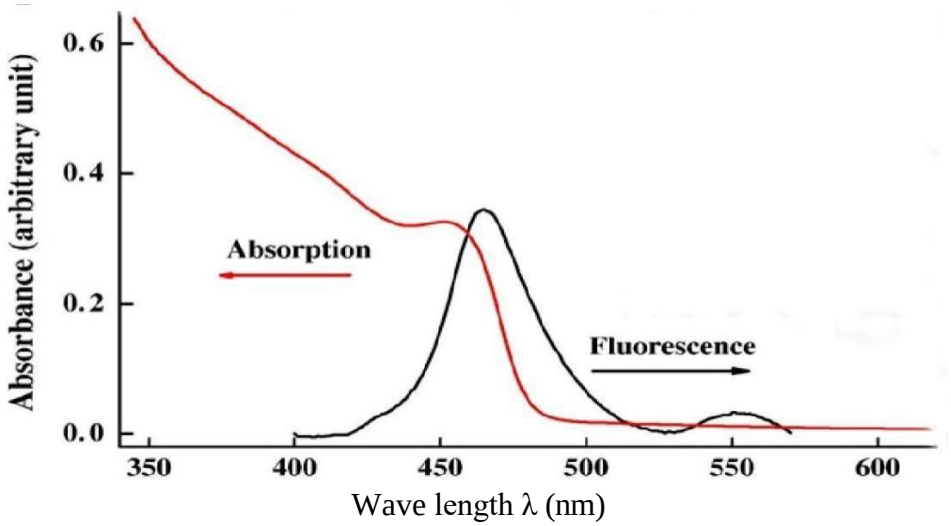
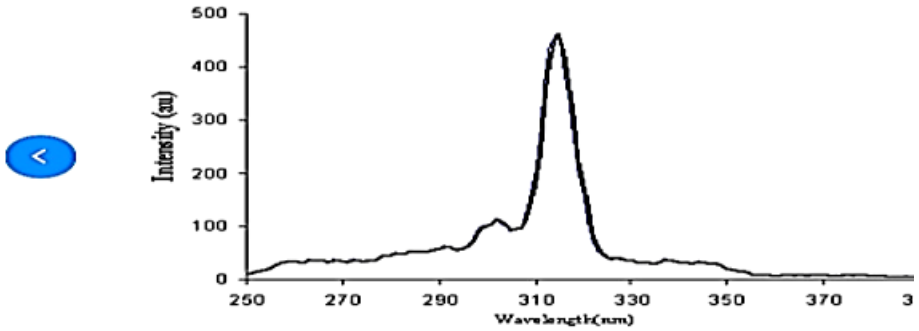


Fig.-5 : Absorption and Emission Fluorescence spectra of CdS-NPs

Photoluminescence for the sample is obtained for CdS nanostructures in various excitations wavelengths (A:280 nm, B:300nm, and C:320 nm) shown in Fig.-6.



Photoluminescence emission spectrum c
nanoparticles.

Fig.-6 : Photoluminescence emission spectrum of CdS-nanoparticles.

Luminescence is maximum at excitation wavelength 320 nm. A strong absorption in the U.V. region was observed at wave length about 460 nm, which was fairly blue shift from the absorption edge of bulk size cadmium sulfide (Fig.-7).

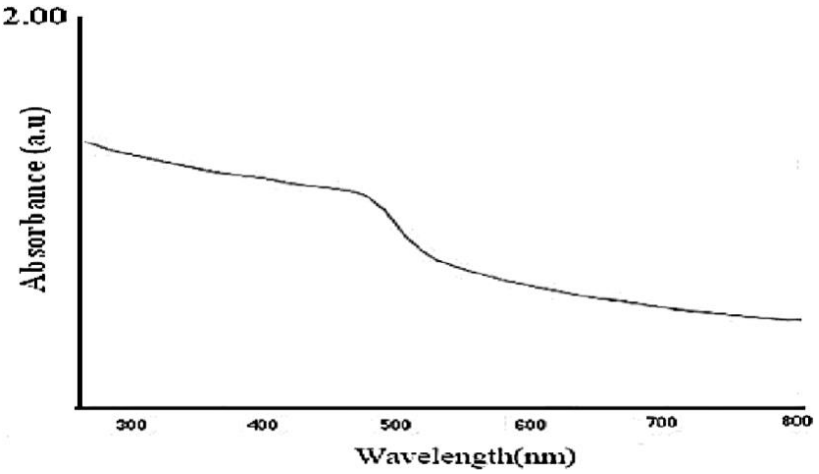


Fig.-7 : UV-spectrum of CdS-NPs.

FTIR spectrum of the precursor with that of the FTIR spectra (Fig.-8) obtained for dried CdS nanoparticles, small peak near 400-470 cm-1 indicates the formation of CdS nanoparticles as this region was assigned to metal sulphur bond. The peak at 405cm-1 corresponded to the characteristic peak of CdS FTIR assignment of CdS nanoparticles.

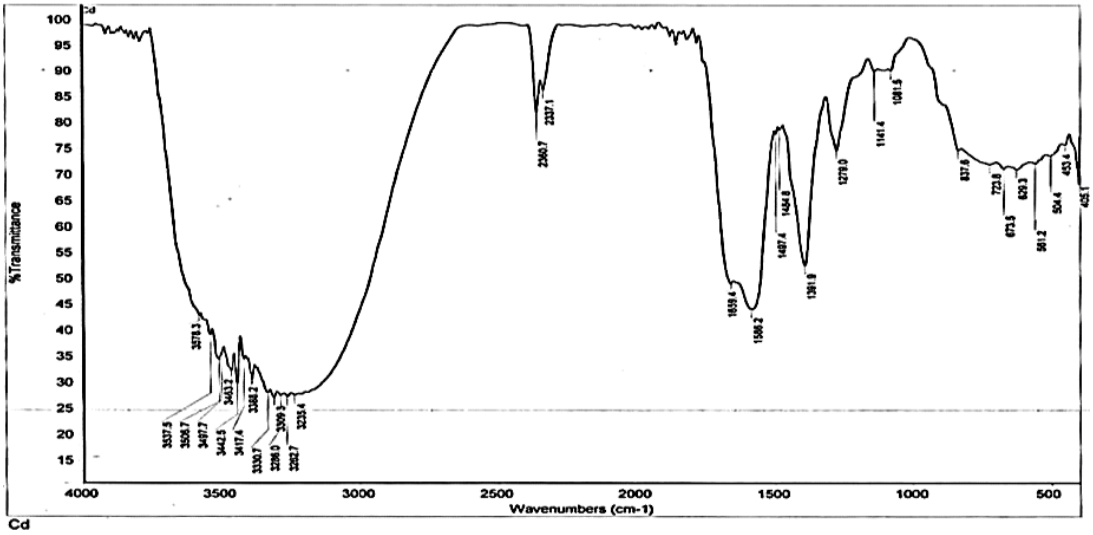


Fig.-8 : IR-spectrum of CdS-NPs

Conclusion :

In the present work, CdS nanoparticles have been successfully synthesized using microwave irradiation of dithiocarbazate ligand as a single molecular precursor source. The use of DMSO for microwave irradiation helps to decompose very fast in the form of small spherical particles. The XRD analysis shows the formation of hexagonal structure. The peak at 405 cm^{-1} corresponded to the characteristic peak of CdS FTIR spectra. UV region was observed at wave length about 345 nm, which was fairly blue shift from the absorption edge of bulk size CdS. Sem and TEM image showed, CdS nanocrystallines are small spherical particles. The particle size and degree of CdS nanoparticles increased with increasing in irradiation time, not affected by the initial CdS molar ratio.

References :

1. P. Simon, Y. Gogots B.Dunn, science.343(2014) 1210-1211.
2. M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, Nanoscale.5(2013) 72-88.
3. I.P. Deshmukh, S.G.Holikatti,P.P.Hankare, J.Phys.D:Appl.Phys.27(1996)1784.
4. M. Yosef, A.K.Schaper, M. Froba, S. Schlecht. Inorg.Chem. 44(2005)5890.
5. N.G. Kedarnath, L.B. Kumbhare, V.K. Jain, P.P.Phadnis, M. Nethaji. Daton Trans (2006) 2714.
6. D. Barreca, A. Gasparotto, C.Maragno, R. Seraglia, E. Tondello, A.Venzo, V. Krishnan, H. Bertagnolli. Appl.Organomet.Chem.19(2005)59.
7. J.C. Bruce, N. Revaprasadu, K.R. Koch, NEW J. Chem. 31(2007)1647.
8. P.S. Nair, G.D. Scholes, J. Mater,Chem. 16(2006) 467.

9. N. Molto, N. Revaprasadu, M.J. Molto, P.O' Brien, N. Heliwell, Polyhedron 26(2007) 3947.

10. M. Lazell, P.O'Brien. Chem. Comm. (1999)2041.

11. C. Byron, M.A. Malik, P.O'Brien, APJ.White, D.J. Williams. Polyhedron 19(2000)211.

12. X. Chen, Z. Zhang, J. Liu, Y.Qian. Chem. Phys. Lett. 407(2005)482-486.

13. S.K. Meher, P. Justin, G. Ranga Rao, ACS Applied Materials & Interfaces 3(2011) 2063-2073.

14. C. Yuan, X. Zhang, L. Su, B. Gao, L. Shen. Journal of Materials Chemistry 19(2009) 5772-5777.

15. F.Dang, K. Kato, H. Imai, S. Wada, H. Haneda, M. Kuwabara: Ultrason Sonochem. 7(2)(2010)310-314.

16. W. Tu, H. Liu : Chem. Mater.12(2), (2010) 310-314.

17. C. Feldmaann and Christ of Metzmacher. J. Mater. Chem. 11(2001) 2603-2606