Synthesis, Characterization and Application of Nanoparticles of Sulfide of Zn^{2+}, Cd^{2+} and Hg^{2+} ions by Using Biogenic and Chemical Route

C. P. Gupta[1], Lakshmi[2], N. Srivastava[3], S. Shukla[4]. A. K.Yadav[5]

[1]Chemistry Department, St. Andrew's College Gorakhpur-273001, U.P. India

[2]Retired Professor, Department of Chemistry D.D.U. Gorakhpur University-273009 UP India

Abstract: ***The preparation of nanoparticles of Zn^{2+}, Cd^{2+} and Hg^{2+} has been carried out by chemical and biochemical route using solvothermal method in presence of reducing solvent, ethylene glycol. In biochemical route, the fungus Aspergilus niger has been used. This reduces SO_4^{2-} ion to S^- forming ZnS, CdS and HgS nanoparticles extracellularly. Electrical conductivity experiment shows a voltage of 6.6mV and a current of 0.18μA. UV- Visible spectra show charge transfer bands at 354nm due to electron transfer between M (d^{10} s^0) ← ($3p^4$), in delocalized band. IR spectrum of the nanoparticles ZnS, CdS and HgS in ethylene glycol by chemical route and by biochemical route shows ν C - H band which was affected in biochemical route from chemical route. The IR spectrum of ZnS in toluene shows the surface modification by formation of stable nanoparticles which clearly indicates the stability by existence of sharp splitting at 3852, 3733 cm^{-1} instead of broad band at 3400 cm^{-1} in ethylene glycol by biochemical route. Similar results have been observed for CdS and HgS in ethylene glycol and toluene solvent respectively. The alkane thiol stabilized nanoparticles transferred to assemble toluene phase obtained is as closed packed hexagonal array shown in X- ray diffraction pattern by evaporation of toluene. TEM show appearance of nanoparticles of ZnS, CdS and HgS in the range 10 to 20nm.***

Keywords: Bio-genic route, Solvothermal method, Aspergillus niger, Nanoparticles. Electrical conductivity, UV-visible, IR spectra, TEM Photograph

1. Introduction

Stable quantum dots of CdS were formed extracellulary by challenging the sulfide ions with aqueous $CdSO_4$ solution. The quantum dots are formed by the reaction of Cd^{+2} ions with sulfide ions due to enzymatic reduction of sulfate ions. The fungus thus plays the role of an enzyme source. In this case, sulphates enzyme is produced by the fungus[1]. CdS nanoparticles were synthesized intracellulary by Schizosaccharomyces pombe strain [2] challenged with 1mM cadmium ion in solution. Biogenic nanoparticles in the size range 1-15 nm were used in the fabrication of a hetrojunction. Yeast cell exhibit ideal diode characteristic. The nanoparticles of CdS, a semiconducting materials, exhibited an absorbance maximum at 305 nm while C.N.R.Rao. et al. reported [3,4] at 450 nm. Mechanism of reduction of nanoparticles by ethylene glycol [5-7] has already been reported by Sridhar et al. In solvent n-propanol, $(CH_3)_2CHOH$ the electron are released [8] and following reaction takes place. $(CH_3)_2CHOH \rightarrow \text{Acetone} + 2H + 2e$. These electrons reduced the nanoparticle of Cd^{+2} ion to Cd^0 and $2H^+$ ion, makes the solution acidic and changes the pH from 9.7 to 1.2. UV- Visible spectrum of CdS in n-propanol showed λ_{max} at 345nm. Keeping all these points in view cadmium sulphate and sodium sulfide are refluxed with ethylene glycol 180 ^{0}C which creates reducing and stabilizing condition. This reaction has not been investigated so far, by stabilizing nanoparticles of ZnS, CdS and HgS,[9] in presence of $Na_2S.7H_2O$ and reducing nature solvent ethylene glycol (EG). The solvothermal method [10] has been used for the synthesis of nanoparticles by chemical route. Lakshmi et.al. [11] have reported the application of ZnS in fabrication of solar cell. Nanoparticles of ZnS , CdS and HgS have also been synthesized by biogenic route using Aspergillus niger species[12,13]. Nanoparticles of ZnS, CdS and HgS have also potential importance for photoionic[14] crystal, IR window, when dipped with additional ions, are used as luminescent materials. Therefore present paper reports the preparation, characterization and application of such interesting nanoparticles of ZnS, CdS and HgS by chemical and biochemical routes. For biochemical routes, the Fungus Aspergilus niger, has been used.

2. Experimental

Zinc Sulphate (ZnSO4), Cadmium sulphate (CdSO4) and Mercury sulphate (HgSO4) of A. R grade, (Emerk) sodium sulfide $Na_2S.\ 7H_2O$ Purity 99.8 was used for preparing nanoparticles by chemical as well as Biochemical route. The Biosynthesis of nanoparticle of sulfide of Zn^{+2}, Cd^{+2} and Hg^{+2} ion by using fungus Aspergilluis niger has been carried out by taking fresh culture of Aspergillue niger and potato dextros agar slant at 25^{0}C. The fungus was grown in 500 ml Erlenmeyler flask each containing 100 ml MGYP medium composed of malt extract (0.2%), glucose (1.0%), Yeast extract (0.3%) and Peptone (0.5%) at 25-28^{0}C in shaking condition of 96h. After 4 days of fermentation, mycelia were separated from the culture broth by centrifugation (5000 rpm) at 10^{0}C for 20 min and settled mycelia were washed trice with sterile distilled water. Ten grams of the harvested mycelial mass was then resuspended in 100 ml of ZnSO4, $CdSO_4$ and $HgSO_4$ aqueous solution of $1x10^{-3}$ M concentration at pH 6 to 6.5. The sterilized culture medium was spread in nine different petredishes. Fungus was inoculated in these petridishes. In one week colonies were grown and after that 1mM solution of $ZnSO_4$ was poured in three petridishes. Similarly 1mM solution of $CdSO_4$ and 1mM solution of $HgSO_4$ solution was poured respectively.

After 18 days extract from these petridishes were collected in nine different test tube, three for $ZnSO_4$, three for $CdSO_4$ and three for $HgSO_4$ in biological active chamber respectively. The extract was taken out from petridishes of each compound thereafter, poured into a shaker at 28^0 C (200ppm) and reaction was completed as their sulfides (ZnS, CdS and HgS) within a period of 72 h. The biotransformation was routinely monitored by visual inspection of the biomass as well as measurement of UV - Visible spectra from the fungal cell. In chemical route the Metal salts are dissolved in ethylene glycol and refluxed at 200^0C for 10 minute. Then solution of Na_2S in EG poured into refluxed solution. Nanoparticles of ZnS, CdS, and HgS are synthesized very rapidly using either ethylene glycol (EG) and toluene as reducing agent as shown in Fig.1. UV-visible spectra were taken from resultant solution.

A Philips transmission electron microscope CM12 equipped with a LaB_6 cathode and a scanning unit was used for the TEM investigations (λL = 36.784A mm) and measurements were performed at 120 kV. Sample preparation was performed by ultrasonically dispersing powder particles and subsequent use of a carbon filmed copper grid as carrier. TEM photographs have been produced from Transmission Electron Microscope, JEOL 2000 EX JEOL, corporation, Japan. UV visible spectra were performed by UV visible spectrometer model – Hitachi – u – 2000. IR spectra of solutions were run in the range 4000 cm $^{1-}$ to 400 cm^{1-} using polythene container on a Perkin FT-IR spectrophotometer RX- IB UK.

Figure 1 (a): Nanoparticle of ZNS, CdS and HgS by chemical route

Figure 1 (b): Nanoparticle of ZNS, CdS and HgS in toluene in toluene

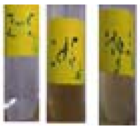


Figure 1 (c): Nanoparticle of ZNS, CdS and HgS by bio-chemical route bby bio-chemical route

3. Result and Discussion

In group analysis one has to create acidic medium and then pass H_2S to get precipitate of CdS while for getting the precipitate of ZnS one has to create basic medium. The precipitation in presence of $Na_2S.7H_2O$ needs none of the pH adjusting solvent. This is the benefit of the reactant $Na_2S.7H_2O$ which is used in reaction as auto adjusting pH reactant. The preparation of nanoparticles of ZnS, CdS and HgS has been carried out by chemical and biochemical route using solvothermal method in reducing solvent as ethylene glycol (EG). Electrical conductivity of solution depend on the potential difference between two electrodes, distance of separation between two electrodes, area of each electrode, number of charged components and their mobility[15]. Throughout the study of first three factors if the first three factors remain the same, then conductivity of solution will depend on the number of the charged component and their mobility. The mobility of the ions depends on their effective size. So a variation in the number metal particles and their size help us to study the properties of the solution by conductometric method. Nucleation growth of nanoparticle of CdS has been controlled by Narayaanan et. al in polymer matrix [16]. Electrical conductivity experiment shows an voltage of 3.6 mV and current of 0.18μA(**Table-1**) which is very small from biogenic synthesis of nanoparticles as explained as plant, fungi and many bacteria[17,18] reduces inorganic sulphate to sulphides to cover their need for the element sulphur. Before the sulphur can be assimilated into biosynthetic pathway it needs to be reduced to **hydrogen sulfide**. Pathway catalyzing the reduction of **sulphate to sulfides** by (i) certain organism can use sulphate as an electron acceptor in absence of oxygen. (ii) pathway of **sulphate reduction** for the purpose of **energy production** are called reduce pathways of dissimulator sulphate reduction. The reduction of **sulphate to sulphite** requires two electron at a standard redox potential (E_0) of -516mV, which is too much for physiological electron carriers. APS lowers the potential to (E_0) = -60mV which is easily covered by thiols. In our reaction Na_2S also produces NaSH (thiol) which also favors the reaction. It is well known that thiols binds to quantum dots of CdS and therefore, it should be possible to phase transfer of aqueous CdS nanoparticle into organic solutions by complexation with R of alkane thiols ($C_2H_5OH + NaSH \rightarrow C_2H_5SH + NaOH$). Biphasic mixture of CdS sol and alkane thiol in toluene resulted in the rapid transfer of CdS nanoparticles in organic (toluene) phase. The alkane thiol stabilized colloidal nanoparticles transferred to assembled toluene phase obtained is as closed packed hexagonal arrary of the nanoparticles (shown in x-ray diffracton pattern) by evaporation of toluene (Fig.2). A concentrated solution of the different sized thiol stabilized CdS nanoparticle were placed on glass substrate (plate) and the particles assembled on the surface. The d- spacing obtained from the low angle peaks are also observed in diffractogram. The low angle diffraction peaks arises from the self assembled arrangement of CdS nanoparticle in the array formed by solvent (toluene) evaporation. It is observed that the separation between clusters decreases as the size of the nanoparticle is reduced as shown in UV- Visible spectra (Fig.3a, 3b). Nanoparticle of CdS in toluene indicated the surface plasmon resonance from the colloidal CdS particles centered at 354nm. CdS synthesized by chemical route show charge transfer band at 390nm which is shifted to 290nm in biochemical route indicating the poor delocalization of the electron of CdS ($3d^{10}$ $4s^0$) ← ($3p^4 3s^2$). IR spectra of the compound ZnS in ethylene glycol by chemical route (Fig. 4a) and by biochemical route (Fig.4b) show ν C-H band around 2358 cm^{-1} and ν band at 1698 cm^{-1}are affected in biochemical compound. The IR spectrum of ZnS in toluene(Fig.4c) shows the surface modification by formation of stable nanoparticles which clearly indicates the stability by existence of sharp splitting at 3852, 3733 instead of broad band at 3400 cm^{-1} in ethylene glycol. Similar results have been observed for CdS and HgS in ethylene glycol and toluene (Fig.5a.5b, 5c and Fig.6a, 6b, 6c) solvent respectively. TEM images have been recorded from the self assembled ZnS, CdS and HgS nanoparticles monolayer obtained by solvent (toluene) evaporation. The larger particle of mean diameter 4 nm is assembled into regular, closed packed domain. Assemblies of smaller nanoparticle show a large fraction of voids within the domain. TEM (Fig.7) shows appearance of nanoparticles of ZnS, CdS and HgS from 10 to 20 nm range.

4. Conclusion

Nanoparticles of sulfide of metal ions are formed as byproduct during conversion of sulphate to sulfide in presence of fungus Aspergillus niger.

Table 1: Conductivity of solution of ZnS, CdS and HgS in ethylene glycol and water (1:50)

Solution	mV		kΩ		μA	
	Chemical route	Biochemical route	Chemical route	Biochemical route	Chemical route	Biochemical route
H_2O (dist.)	3.1	3.0	3.4	3.1	0.23	0.25
ZnS	3.7	3.6	2.9	2.8	0.17	0.18
CdS	3.6	3.5	3.0	2.9	0.18	0.19
HgS	3.8	3.7	3.2	3.4	0.16	0.17

Table 2: Data of electronic spectra of solution of ZnS, CdS and HgS in ethylene glycol and water (1:50)

Chemical compound	λ_{max}		OD		Type of transition
	Chemical route	Biochemical route	Chemical route	Biochemical route	
EG	242	240	0.809	0.810	
ZnS	283	286	1.247	1.241	Charge transfer
EG	223	220	0.812	0.819	
CdS	390	290	1.374	1.371	Charge transfer
EG	215	210	0.805	0.801	
HgS	356	350	1.394	1.391	Charge transfer

Reference

[1] M. Sastry, A. Ahmad, P. Mukherjee, .Mandal, J Am. Che. Soc., **24** (2002)12108-9.

[2] M. Kowshik, N. Deshmukh, W.Vogel, J. Urban, S. K. Kukarni and K. M. Paknikar. Biotechnol Bioeng, 78(**5)** (2002)583-588.

[3] C. N. R. Rao, Ved Varun, Agrawal, G.U. Kulkarni, P. John Thomas, U. Gautam and M.Ghosh. Current Science, 85(**7)** (2003)1041-3.

[4] C. N. R. Rao, G.U.Kulkarni, P.John Thomas, P. P. Edward, properties of size of nanoparticles, Chem. Eur.J., **8** (2002), 2935.

[5] T. Teranishi, R. Kurita, and M. Miyake, J. Inog. Organometal Pol.**10** (2002)145.

[6] Sridhar Komarneni, Current Science, **85(12)**(2003).

[7] A. Sreekumaran Nair and T. Pradeep, Current Science, **84(12)** (2003) 1559.

[8] F. Fievet, J. P. Hagier, and Z. M. Figlar, MRS Bull, **29**(1989) XXIV.

[9] T. Theivasnthi and M. Alager, Nano Biomed Eng. **3(3)** (2011)163.

[10] P. Toneguzzo, G.Viau, O. Acher, F.Guillet, E, Bruneton, F. Fievet-Vincent and F.Fievet, J. Mater. Sci., **35** (2000) 3767.

[11] Lakshmi, A.Sahay, S.k.Shukla , J.Mater., Sci., **29** (2004) 1325.

[12] H. B. Patil, S. B. Bores, D. H. Patil, U. K. Patil, H. M.Patil, Archieves of Physics microbial Research,2(3) (2011)153-158.

[13] D. Lehningrd Nelson, M. Cox Principle of biochemistry IIn Ed (2011).

[14] Y. Xia, B. Gates, Y.Yin and Y.Lu. Adv. Mater. **12** (2000) 693.

[15] Sujit kumar Ghosh, Navnita Sharma, Madhuri Mandal Subrata Kundu , Kesumi and Tarasanker Pal, Current Science, **84** (2003)6791.

[16] S. Ramesh, V. Narayanan, Chem. Sci.Trans. 2(81) (2013)8192-8194.

[17] CH. Lilling, S. Schiffmann, C. Berndt, A. Berken, R. Tischka, J.D. Schwennarch, Biochem Biophy, **392 (2)** (2001) 303-10.

[18] C. Berndt, CH. Lilling, M. Wollengenberg, E. Bill, M.C. Mansilla, D. De Mendoza, A. Seidler, J.D. Schwenn, J Biol. Chem., **27(9)** (2004) 7850-5.

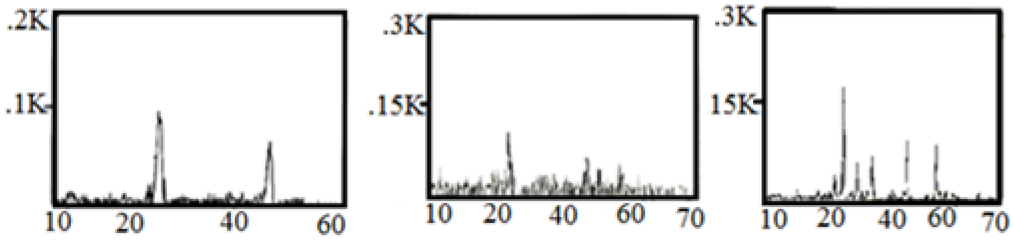


Figure 2: XRD pattern of ZnS, CdS and HgS nanoparticles by biochemical route

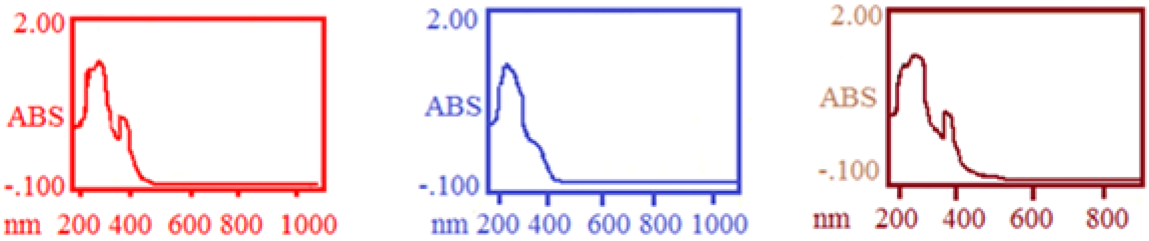


Figure 3(a): UV Visible spectrum of ZnS, CdS and HgS nanoparticles by chemical route

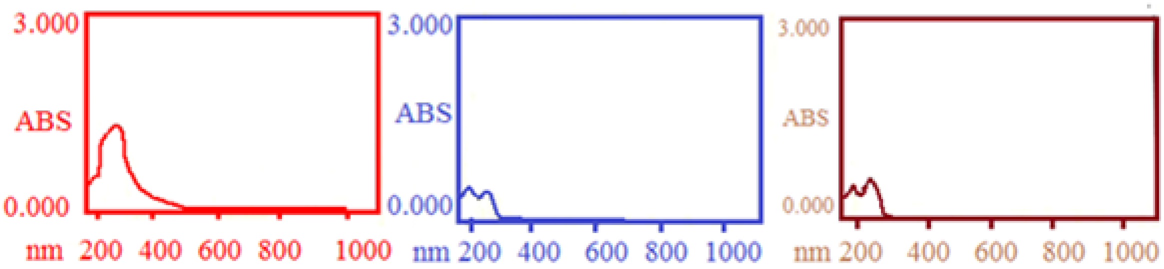


Figure 3(b): UV Visible spectrum of ZnS, CdS and HgS nanoparticles by bio chemical route

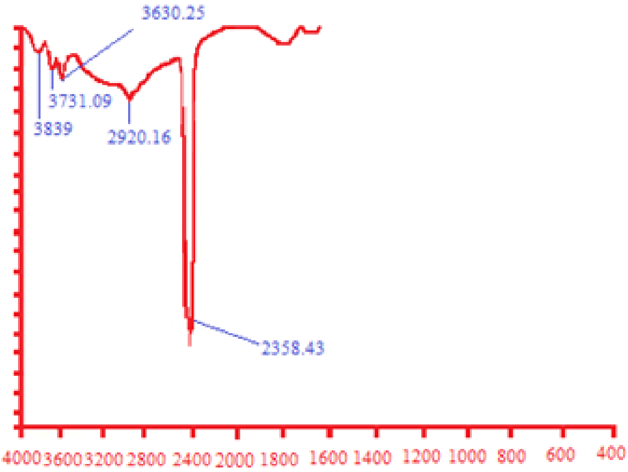


Figure 4 (a): IR spectra of ZnS in ethylene glycol by chemical route

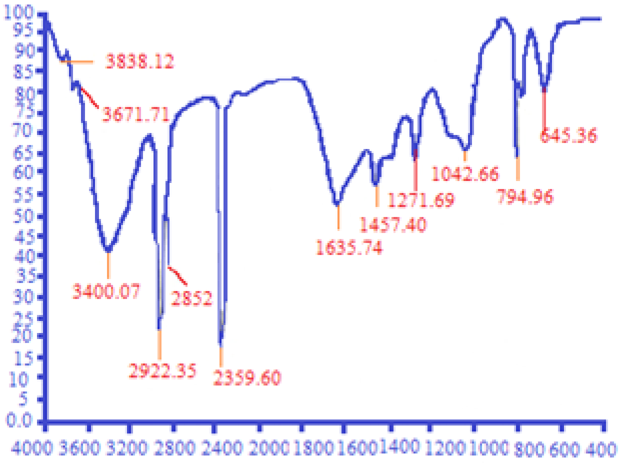


Figure 4(b): IR spectra of ZnS in ethylene glycol by bio chemical route

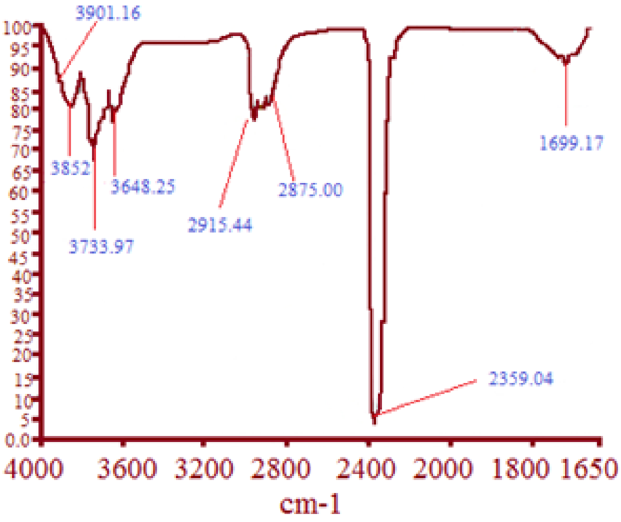


Figure 4(c): IR spectra of ZnS in toluene by chemical route

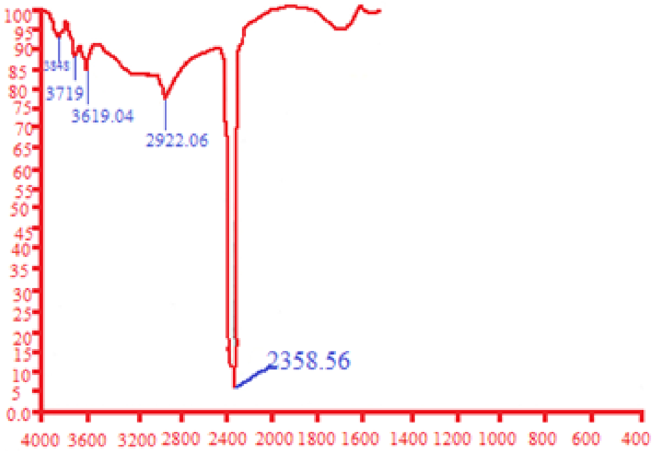


Figure 5 (a): IR spectra of CdS in ethylene glycol by chemical route

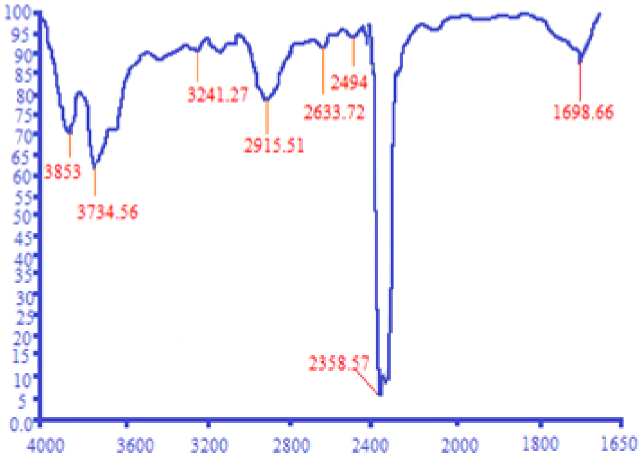


Figure 5(b): IR spectra of CdS in ethylene glycol by bio chemical route

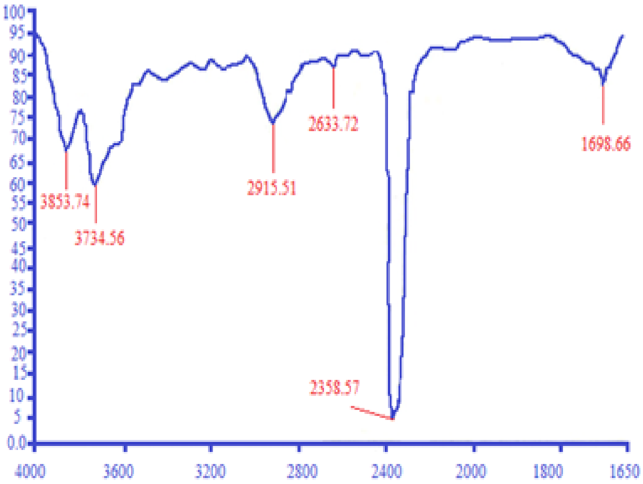


Figure 6(b): IR spectra of HgS in ethylene glycol by bio chemical route

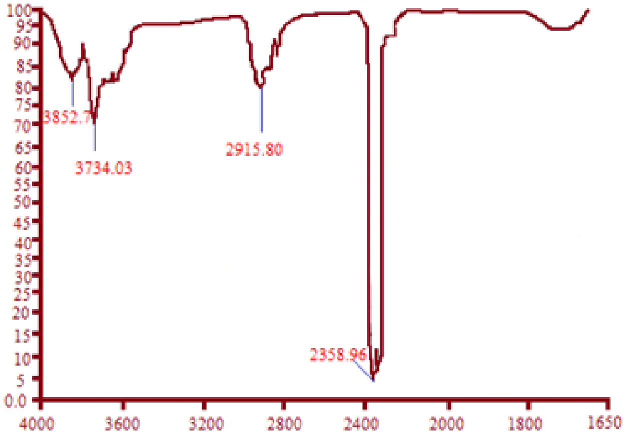


Figure 5(c): IR spectra of CdS in toluene by chemical route

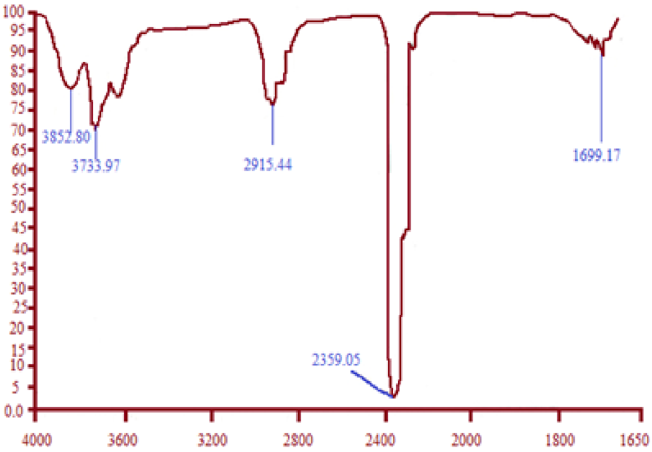


Figure 6(c): IR spectra of CdS in toluene by chemical route

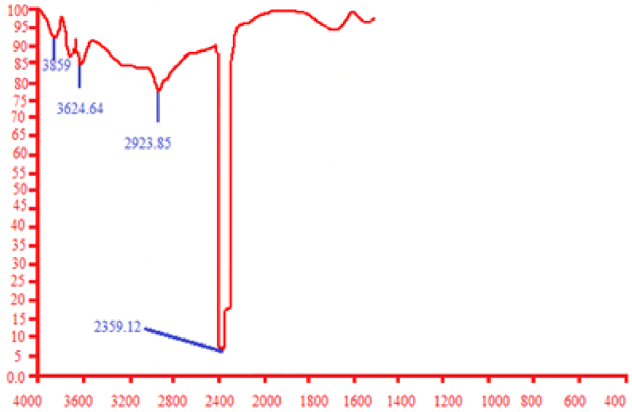
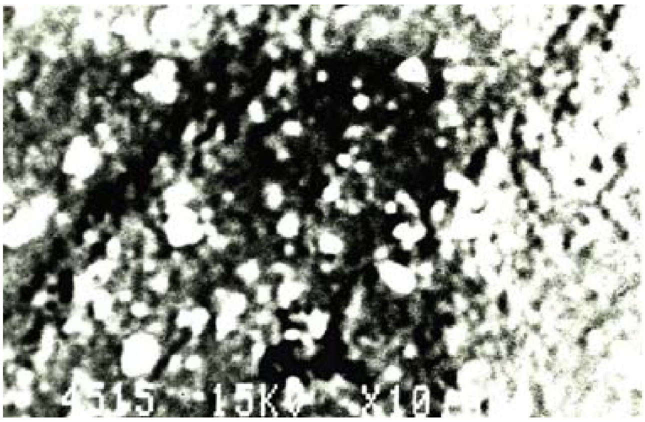
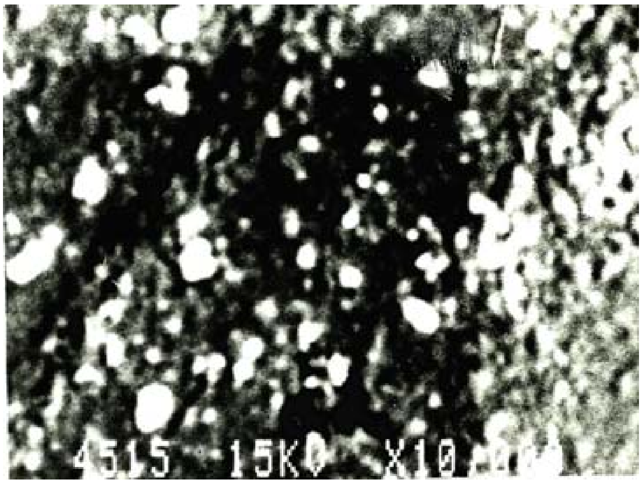


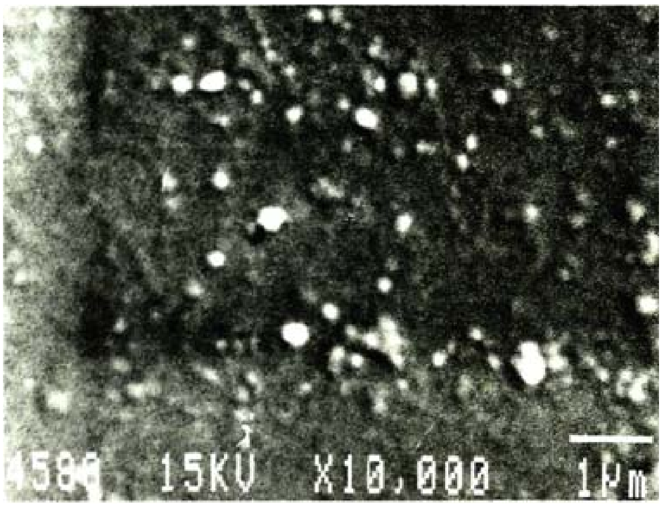
Figure 6 (a): IR spectra of HgS in ethylene glycol by chemical route



(a): ZnS nanoparticle



(b): CdS nanoparticle



(c): HgS nanoparticle

Figure 7: TEM photographs of nanoparticls of (a) ZnS (b) CdS (c) HgS