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

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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 Aspergillus 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$^0$) $\rightarrow$ (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 v 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 3832, 3733 cm$^{-1}$ instead of broad band of 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 extracellularly 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 intracellularly 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 heterojunction. 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$_3$)$_2$CHOH the electron are released [8] and following reaction takes place. \((\text{CH}_3\text{CHOH} \rightarrow \text{Acetone + 2H}^+2e)\). 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 $\lambda_{\text{max}}$ at 345nm. Keeping all these points in view cadmium sulphate and sodium sulfide are refluxed with ethylene glycol 180 °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$_2$S,7H$_2$O 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 Aspergillus niger, has been used.

2. Experimental

Zinc Sulphate (ZnSO$_4$), Cadmium sulphate (CdSO$_4$) and Mercury sulphate (HgSO$_4$) of A. R grade, (Emerek) sodium sulfide Na$_2$S. 7H$_2$O 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 Aspergillus niger has been carried out by taking fresh culture of Aspergillue niger and potato dextros agar slant at 25°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°C in shaking condition of 96h. After 4 days of fermentation, mycelia were separated from the culture broth by centrifugation (5000 rpm) at 10°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 ZnSO$_4$, 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 petridishes. 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 ZnSO₄, three for CdSO₄ and three for HgSO₄ in biological active chamber respectively. The extract was taken out from petridishes of each compound thereafter, poured into a shaker at 28°C for 10 minute. Then solution of Na₂S 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 LaB₆ cathode and a scanning unit was used for the TEM investigations (L = 36.784 Å 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 polyethylene 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

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

### 3. Result and Discussion

In group analysis one has to create acidic medium and then pass H₂S to get precipitate of CdS while for getting the precipitate of ZnS one has to create basic medium. The precipitation in presence of Na₂S.7H₂O needs none of the precipitate of ZnS one has to create basic medium. The IR spectra of the precipitation in presence of Na₂S.7H₂O needs none of the precipitate of ZnS one has to create basic medium. The precipitation in presence of Na₂S.7H₂O needs none of the precipitate of ZnS one has to create basic medium. The precipitation in presence of Na₂S.7H₂O needs none of the precipitate of ZnS one has to create basic medium. The precipitation in presence of Na₂S.7H₂O needs none of the precipitate of ZnS one has to create basic medium.

The reduction of sulphate to sulphides 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 (Eₒ) of -516mV, which is too much for physiological electron carriers. APS lowers the potential to (Eₒ) = -60mV which is easily covered by thiol. In our reaction Na₂S also produces NaSH (thiol) which also favors the reaction. It is well known that thiol 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 (C₃H₆OH +NaSH → C₃H₇SH + NaOH). Biphase 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 array of nanoparticles (shown in x-ray diffraction 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 2- 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 nanoparticles 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 nanoparticles centered at 354nm. CdS synthesized by chemical route charge transfer band at 390nm which is shifted to 290nm in biochemical route indicating the poor delocalization of the electron of CdS (3d⁶ ⁴S⁰) ⇔ (3p³3s²). IR spectra of the compound ZnS in ethylene glycol by chemical route (Fig. 4a) and by biochemical route (Fig.4b ) show v C-H band around 2358 cm⁻¹ and v 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        | Chemical route | Biochemical route | Chemical route |
|                 |       |       |       |
| H₂O (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<sub>max</sub> | OD | Type of transition |
|                 | Chemical route | Biochemical route | Chemical route |
| EG              | 242            | 240     | 0.809 | 0.810 | Charge transfer |
| ZnS             | 283            | 286     | 1.247 | 1.241 | Charge transfer |
| EG              | 223            | 220     | 0.812 | 0.819 | Charge transfer |
| CdS             | 390            | 290     | 1.374 | 1.371 | Charge transfer |
| EG              | 215            | 210     | 0.805 | 0.801 | Charge transfer |
| HgS             | 356            | 350     | 1.394 | 1.391 | Charge transfer |

### Reference


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

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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 biochemical route

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

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

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

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

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

(b): CdS nanoparticle

(c): HgS nanoparticle