Chapter-2

2. Fabrication of DMS nanostructures

Fabrication of DMS nanostructures as described in this chapter was carried out by adopting inexpensive chemical synthesis method. We present here the result of our current efforts on fabrication of transition metal (TM) doped ZnS and ZnO nanocrystals through chemical as well as solid state chemical reaction route respectively. Synthesis of cetyl trimethyle ammonium bromide (CTAB) assisted TM (Mn,Co,Ni) doped ZnO nanostructures were carried out by adopting solid state chemical reaction route at room temperature. We found elongated nanostructures for all TM:ZnO systems in the form of powder. Study was carried out by fabricating TM:ZnO samples with three different TM concentrations ranging from 1% to 5%.

Gamelin et al [191] reported the synthesis of colloidal Mn$^{+2}$ doped ZnO (Mn$^{+2}$:ZnO) quantum dots at room-temperature and the preparation of ferromagnetic nanocrystalline thin films by hydrolysis and condensation reaction in DMSO under atmospheric conditions. Gamelin’s group proposed that direct chemical syntheses of ZnO DMSs can provide better control over material composition than is obtained with some high-temperature vacuum deposition or solid-state synthesis techniques. The same group reported robust, high-$T_c$ in thin films of these nanocrystals prepared by spin coating at 300 K. The corresponding coercivity was 92 Oe, approximately.

Polyvinyl alcohol (PVA) embedded Mn:ZnS and Cr:ZnS spherical nanostructures have been developed at room temperature by adopting low cost chemical synthesis route. As synthesised TM:ZnS nanostructures were found in the form of colloidal solution. Study of Mn:ZnS system was done by varying Mn concentration ranging from 0.008% to 0.25%. Along with PVA,
another surfactant Polyvenyl Pyralidone (PVP) has been utilised to develop Cr:ZnS system.

Only few synthesis processes of colloidal nanoparticles have been reported in the literature. Colloidal nanocrystals should form ideal hosts for strongly-confined artificial atoms, i.e. configuration of one to a few electrons occupying the conduction energy levels in the nanocrystal. Such nanocrystals can be obtained in molar quantities by wet chemical synthesis with increasing control of the size, shape and surface electronic properties.

2.1 Materials

From the application point of view, the large scale synthesis and long term preservation of as synthesised nanoparticles are very much important. In order to increase the stability of the nanoparticles and to protect from the environmental attack they are to be embedded with glass, zeolite or polymer [192]. Surfactants usually play an important role in the electrolysis process to bring some properties of the electro-deposited layer, such as the brightness, moistness, smoothness, and homogeneity.

(i) Cetyl trimethyle ammonium Bromide (CTAB)

For fabrication of Transition metal doped ZnO nanostructures we have utilized CTAB as a surfactant. The surfactant CTAB (cetyl trimethyl ammonium bromide) is a cationic surfactant. It was considered as having good potential in the application of nano-technology because of its strong adsorbed ability in nano particles [193-195]. Besides, the CTAB is also suitable for being as a corrosion inhibitor [196-198]. The two ends of each CTAB molecule has two specific properties, one end with high positive property is hydrophilic (head), while the other end is hydrophobic (tail). In water the hydrophilic end (ion head) repeal each other due to long range electrical force and hydrophobic end (tail chain) attract each other due to short range Vander-wall force promoting
micelle formation by the CTAB molecule. The number of molecules present in a micelle once, the critical micelle concentration (CMC) has been reached. At room temperature (~30°C), CTAB forms micelles with aggregation number 75-120.

(ii) Polyvinyle Alcohol (PVA/PVOH)

Polyvinyl alcohol (PVA) is an odourless and tasteless, translucent, white or cream colour granular powder. Generally, it is used as a moisture barrier film for food supplement tablets and for foods that contain inclusions or dry food with inclusions that need to be protected from moisture uptake.

By adopting chemical synthesis route we have fabricated polyvinyl alcohol (PVA) assisted Mn and Cr doped ZnS nanostructures. PVA has excellent emulsifying, film forming, and adhesive properties. It is also resistant to oil, grease and solvent. It is odourless and nonotoxic. It has high flexibility and tensile strength as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity. PVA absorbs more water with higher humidity. The water, which acts as a plasticiser, will then reduce its tensile strength. PVA is fully degradable and a quick dissolver. However, in cold water, it dissolves slowly, but with application of heat it dissolves quickly. PVA has a melting point of 230°C and 180-190°C for the fully hydrolysed and partially hydrolysed grades. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. PVA is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it.

PVA is a good protective colloid for aqueous emulsions and is employed for this purpose in a large variety of emulsion and suspension systems. It also finds use in wet strength adhesives.

The PVA matrix is presented as,

\[
\left[ \begin{array}{c}
\text{CH}_2 \\
\text{CH} \\
\text{OH}
\end{array} \right]^n
\]
Polyvinyl Pyrrolidone (PVP)

We have also fabricated Cr doped ZnS nanostructures by utilizing another polymer matrix Polyvinyl Pyrrolidone (PVP) for further investigation. Polyvinyl pirrolidone (PVP) is an excellent polymer with remarkable combination of properties (details are given in the appendix). It has variety of properties, such as: Transparency, adhesive and cohesive, protective colloid and suspending agent, film former, chemical and biological inertness, low toxicity, high media compatibility, cross linkable flexibility etc..

The PVP matrix is given by:

![Polyvinyl Pyrrolidone Structure](image)

2.1.1 Fabrication of Bare ZnO nanostructures

For fabrication of bare ZnO nanostructures the the materials utilized are;

i. Zinc acetate dehydrate (ZAcD): [Zn(CH₃COO)₂·2H₂O];

ii. Cetyle trimethyle ammonium bromide (CTAB): [C₁₉H₄₂BrN];

iii. Sodium hydroxide flakes: NaOH.

All reagents were of analytical grade (99.99 % purity) and were used without further purification. Bare ZnO nanoscale systems were fabricated by adopting a solid state chemical reaction route. Zinc acetate dehydrate (ZAcD), Cetyle trimethyle ammonium bromide (CTAB) and Sodium hydroxide flakes (NaOH) are mixed by keeping their molar ratio as 1:0.5:2. The mixture was ground gently in a mortar at room temperature for few hours (~2 hrs) till a paste like compound is obtained. The mixture was repeatedly washed with double distilled water and then annealed at 60°-80° C for about 4-5 hrs. After
washing with double distilled (DD) water the as-synthesised product was dried and the final product was obtained in the form of powder.

2.1.2 Fabrication of TM doped ZnO nanostructures

We have adopted solid state chemical reaction route to fabricate TM(Mn,Co,Cr,Ni) doped ZnO nanostructures. Acetates of Zn and TM taken in the appropriate molar ratio to obtain three samples from each TM as 1at.% TM, 3at.% TM and 5at.% TM. The acetates of Zn and TM were ground gently in a mortar at room temperature for ~ 2 h. Sodium hydroxide flakes and cetyl trimethyl ammonium bromide (CTAB) were mixed in the precursor and grinded for several hours till a paste like compound is obtained. The mixture was repeatedly washed with double distilled water and then annealed at 60\textdegree{}-80\textdegree{}C resulting in TM doped ZnO nanostructures in the form of powder. According to the TM concentrations in the samples (1%, 3% and 5%), they were indexed as TM-1, TM-3 and TM-5. A part of the as-prepared powdered sample was kept for XRD, PL, FTIR, EDX and HRTEM studies and another part was kept for pellet preparation to carry out magnetic characterization. The powdered samples were pressed into pellets of about 3-4 g by weight and 10 mm in diameter at a pressure of 6 tons/cm\textsuperscript{2}.

2.1.3 Fabrication of TM doped ZnS nanostructures

(i) Mn doped ZnS

ZnS:Mn nanoaggregates are fabricated by adopting simple, low cost chemical route using polyvenyl alcohol as desired matrix. For this, 2.5wt% Poly vinyl alcohol (PVA) was prepared by using Double distilled water and Magnetic stirrer with stirring at ~200 rpm at a constant temperature of 65\textdegree{} until a transparent solution is formed. Zinc chloride(aq) and manganese chloride(aq) solutions were prepared separately and then they were stirred in a mixed environment with variable Mn: Zn ratio (Mn conc. 5% - .008%).
Figure 2.1: Flow chart showing synthesis route of ZnS:Mn nanostructures embedded in Polyvinyl alcohol (PVA) matrix.

The as prepared precursor was mixed with PVA matrix under stirring. Into this dropwise injection of Na$_2$S (.01M) solution led to the growth of ‘ZnS:Mn’ nanoparticles. Figure 2.1 shows the flow chart of the chemical route for synthesis of the “ZnS:Mn in PVA” system.

Out of eight samples prepared with different Mn:Zn molar concentrations within the range 5at.%Mn to 0.008at.%Mn, three samples 0.25at.%Mn, 0.188at.%Mn and 0.008at%Mn were selected on the basis of their preliminary investigations carried out with UV-Vis ans Photoluminescence spectroscopy and indexed as A, B and C for further investigations. Fluid samples were collected for UV-VIS study and TEM measurements while thin films were casted on glass slides for photoluminescence study, AFM, MFM and XRD investigations.
(ii) Cr doped ZnS

Cr doped ZnS encapsulated in polyvinyl alcohol (-C₂H₄O)n and Polyvinyl pyrrolidone k30 (C₆H₉NO)x was fabricated using a low cost colloidal solution casting route. For fabrication of Cr doped ZnS nanostructures in PVA matrix, we have followed exactly the same route as described above for Mn doped ZnS system, only manganese chloride(aq) has been replaced by chromium chloride(aq). In case of Cr doped ZnS in Polyvinyl pyrrolidone (PVP) matrix, the organic host PVP was taken in place of PVA. For this, 2% (w/v) PVA/PVP) in double distilled water were magnetically stirred at ~200 rpm at a constant temperature for six hours separately until a transparent solution were formed. Next, 0.1 M ZnCl₂ was added to the dielectric hosts under stirring condition and then 0.01M Cr₂O₃ solution was mixed at room temperature in both matrices. Finally 0.1 M Na₂S solution was drop wise injected to the two precursors, which led to the growth of ZnS:Cr nanostructures in PVA and PVP.

Conclusions

- CTAB assisted Bare ZnO as well as TM (Mn,Co,Ni) doped nanostructures have been fabricated successfully by adopting simple, inexpensive solid state chemical reaction route.
- PVA and PVP embedded Bare and TM (Mn,Cr) doped ZnS nanostructures were developed by adopting chemical synthesis method.