

# Luminescence of ZnS Nanoparticles in Organic Phase And Effect Of Doping

Usha Raghavan<sup>1</sup>, Balaprasad G. Ankamwar<sup>2</sup>, Murali Sastry<sup>3</sup>

*Information Technology Department<sup>1</sup>, VPM's Polytechnic<sup>1</sup>*

*Chemistry Department<sup>2</sup>, Pune University<sup>2</sup>*

*Director-Innovation<sup>3</sup>, DSM<sup>3</sup>*

*Email: usharagha@gmail.com<sup>1</sup>*

**Abstract-** The present work provides a potentially efficient and a simple chemical route for the synthesis of ZnS & Zn<sub>(1-x)</sub>Mn<sub>x</sub>S nanocrystals in organic phase at ambient room temperature. The nanostructures of the prepared undoped ZnS and Mn<sup>2+</sup> doped ZnS:Mn nanoparticles have been analysed using UV-Vis spectrophotometer and Fourier Transform Infrared studies have been studied. There is a wavelength shift in the emission of manganese doped samples. The size and shape of the synthesized nanoparticles have been studied using the Transmission Electron Microscope.

Chemical manipulation towards both size and shape tunable preparation is achieved successfully.

**Index Terms-** Quantum confinement; absorption; emission; Doping; Capping agent; organic phase.

## 1. INTRODUCTION

Development of synthesis protocols for nanomaterials over a range of sizes, shapes and chemical compositions is an important aspect of nanotechnology. In recent years, we have witnessed impressive advances in understanding the unusual physico-chemical and opto-electronic properties of nanomaterials, their synthesis, assembly and packaging for commercial applications [1]. One important area of nanotechnology is involved in the development of reliable processes for the synthesis of nanomaterials over a range of sizes with good monodispersity and chemical composition [2]. Due to high surface area, the nanostructured materials possess a high surface energy and therefore are thermodynamically unstable or metastable. One of challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the aggregation of nanomaterials. Due to high surface energy of the nanoparticles, they are extremely reactive and most systems without protection or passivation of their surfaces undergo aggregation [3]. Organic stabilizers are usually used to prevent nanoparticles from aggregation by capping their surfaces [4].

Metal nanoparticles have attracted considerable interest in fields such as optics and catalysis, because of their size and shape dependent physico-chemical properties [5]. Among such procedures, those that require an aqueous medium are the most convenient to develop because of water's ability to solubilize a variety of ions and stabilizing molecules. On the other hand, nanoparticles prepared in organic media are interesting for applications to catalytic processes and for surface modifications with organic functional

groups to fine tune their properties [5-8]. Differently sized and shaped metal nanoparticles can be obtained in organic media either by preparing them directly in those media [9] or by transferring nanoparticles from aqueous phase to organic phases [10-13]. The first approach is very sensitive and difficult to achieve convenient size and shape controllable processes. The second approach has the advantage that there are many well developed procedures available for the preparation of well-defined metal nanoparticles in aqueous media.

Phase transfer of metal nanoparticles from aqueous phase to an organic phase can be achieved by capping the nanoparticles with thiols and amines [10], or by using phase-transfer reagents, such as surfactants to improve the solubility of nanoparticles in organic media.

ZnS, which is an important wide band gap semiconductor, has attracted attention owing to its wide application including UV light emitting diodes, organic LEDs, efficient phosphors in flat panel display, photovoltaic devices etc [10]. To utilize semiconductor nanostructures as building blocks of functional nanodevices, it is important to synthesize them by having in the end diverse physical properties. This could be realized via appropriate doping. Transition metal ions doped ZnS nanoparticles are the most popular materials for research in semiconductor nanocrystals. Doped nanocrystals of semiconductor can yield high luminescence [12]. These results suggested that doped semiconductor nanocrystals form a new class of luminescent materials, with a wide range of applications in e.g. displays, sensors and lasers [13]. The paper highlights the method of synthesis of Zinc sulphide nanocrystals in chloroform with Octa Decane Thiol as the capping agent.

## 2. EXPERIMENTAL DETAILS

### 2.1. Chemicals

The following are the chemicals used for preparation of the sample. They are of analytical grade and were used as received.

Zn (NO<sub>3</sub>)<sub>2</sub> -Zinc Nitrate, C<sub>18</sub> H<sub>36</sub> O<sub>2</sub> -Stearic Acid, CHCl<sub>3</sub> – Chloroform, C<sub>18</sub>H<sub>38</sub>S- Octa decane Thiol, MnCl<sub>2</sub> -Manganese Chloride

### 2.2. Sample Preparation

For synthesis, 50 mL of 10<sup>-3</sup>M aqueous Zn (NO<sub>3</sub>)<sub>2</sub> whose pH is adjusted to 8.5 is mixed with 50 mL of 10<sup>-3</sup>M stearic acid in chloroform. The mixture is stirred vigorously using a magnetic stirrer for 5 hours at room temperature. The zinc ions from the aqueous phase get transferred into the organic phase. The phase transferred zinc ions present in organic medium is separated from the stirred solution using a separating funnel.

To equal volumes of phase transferred zinc, add 5 x 10<sup>-3</sup> M Octa Decane Thiol (ODT) dissolved in chloroform. ODT behaves as a capping agent so that the Zinc ions do not agglomerate. The solutions are mixed well by shaking and the mixture is kept aside for 15 minutes. Then H<sub>2</sub>S gas is bubbled through the mixture for 15 minutes. As the reaction proceeds, a yellow coloration is observed in the solution, indicating the formation of ZnS particles in organic phase.

For doping with Manganese 10<sup>-3</sup>M solution of MnCl<sub>2</sub> in proportions of 2%, 5%, 8%, 10% are prepared and added along with Zn (NO<sub>3</sub>)<sub>2</sub> solutions.

## 3. RESULTS AND DISCUSSIONS

The room temperature UV-Vis spectra of undoped ZnS and doped ZnS : Mn<sup>2+</sup> samples are shown in Fig 1.(A).

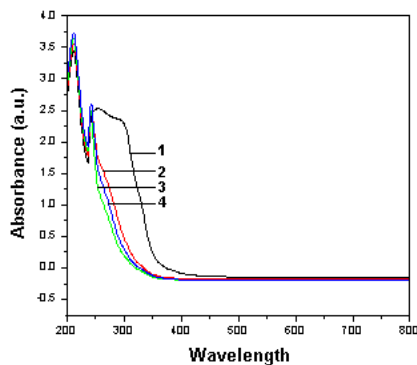


Fig.1(A) shows the UV-visible absorption spectrum of 2% by wt Mn doped ZnS nanoparticles(1), 5% by wt Mn doped ZnS nanoparticles (2), 8% by wt Mn doped ZnS nanoparticles (3), 10% by wt Mn doped ZnS nanoparticles (4)

Fig.1(A) curve 1 represents the absorption spectrum of 2% manganese doped Zinc sulphide nanoparticles, curve 2 represents 5% manganese doped Zinc Sulphide nanoparticles, curve 3 represents 8% manganese doped zinc sulphide nanoparticles and curve 4 represents 10% manganese doped zinc sulphide nanoparticles.

The absorption spectra are recorded in the range of 200-800 nm at room temperature. A strong absorption peak at 215 nm is assigned to the optical transition of the first excitonic state of the Mn doped ZnS nanoparticles and its narrow shape is an evidence of the very small size of the dispersed particles. The maximum absorption edge for the sample is observed at 320 nm which indicate a 25 nm blue shift from the bulk (345 nm). This blue shifted absorption edge is due to the small size of the particles. By doping with manganese ions, the wavelength of absorption edge shift towards a higher wavelength compared to ZnS nanoparticles. This changes the band gap energy suggesting that there is direct energy transfer between semiconductor excited states and 3d levels of the

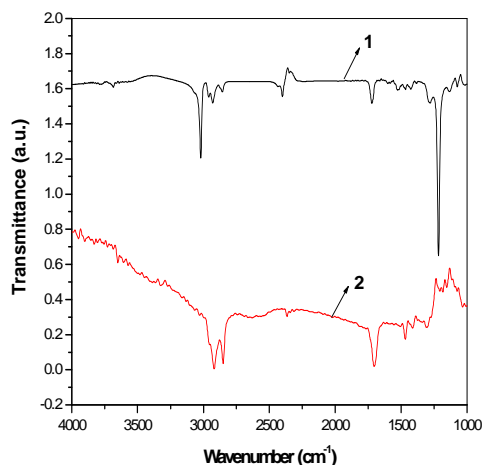


Fig.2 FTIR spectra recorded from drop coated film on Si(111) Wafer of ZnS nanoparticles(1) & 5% Mn doped ZnS nanocrystals(2).

Mn<sup>2+</sup> ions, that are coupled by energy transfer process [14].

FTIR measurements have been made in the wave number range 500 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>.The FTIR characteristics of undoped ZnS and 5% manganese doped ZnS is shown in Fig.2.

Fig.3 shows the High Resolution TEM (HRTEM) micrographs recorded at different magnifications from the as-prepared ZnS nanoparticles in organic phase. It is apparent that the ZnS nanoparticles are spherical in nature. The size of the nanoparticles seems to be in the range of 5-10 nm. The figure shows nearly monodispersed spherical nanoparticles.

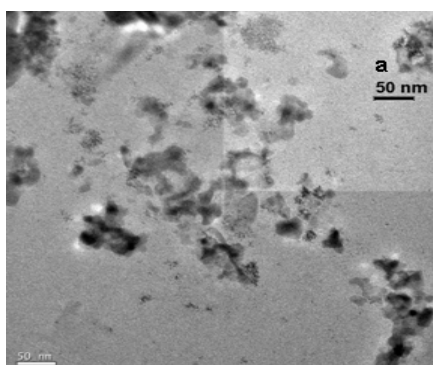
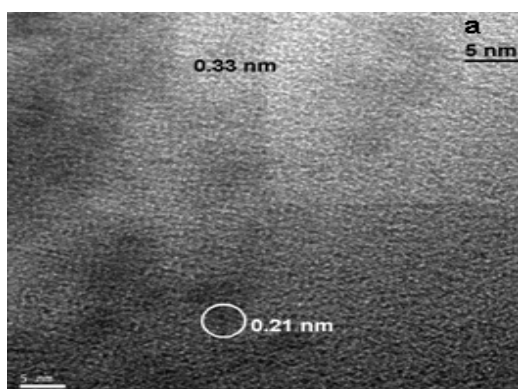


Fig.3 HRTEM micrographs recorded at from as-prepared ODT capped ZnS nanoparticles.

Fig.4 illustrates the High Resolution TEM micrographs 5% manganese doped ZnS nanoparticles. It can be seen that the nanoparticles so synthesized are spherical in shape and show a size of 0.21 nm and 0.33 nm. Doping has reduced the size and made the dispersion of the particles uniform. The highly dense structures clearly points out the strong surface binding of the ODT molecules with the ZnMnS nanoparticles,



thereby restricting their aggregation.

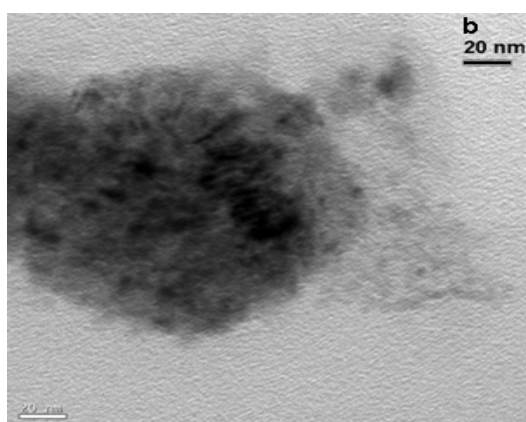


Fig.4(a&b) HRTEM micrographs recorded at different magnifications from a drop cast film of ODT capped Zn<sub>0.95</sub> Mn<sub>0.05</sub>S nanocrystals

#### 4. CONCLUSIONS

Zn ions present in aqueous medium may be phase transferred into non-polar organic solvents by coordination with ODT molecules present in organic phase. The ODT molecules covalently bind to the ZnS nanoparticles surface. The most significant result in this experimentation is development of a system which allows the investigation of subtle surface state interaction and reactions of size quantized ZnS semiconductor particles in organic phase. UV- Vis absorption and the band edge photoluminescence spectra are consistent with narrow size distribution and excellent particle quality. ZnS has good absorption for light in the wavelength of 220-350 nm and this peak position reflects the band gap of the particles. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap of the prepared ZnS nanoparticles. This blue shifted absorption edge is due to small size of the particles. The smaller the size of quantum dots the higher the light emission efficiency they could provide. Therefore it is reasonable to expect that the synthesized products in this work could potentially be used in electroluminescent applications upon doping.

#### References

- [1] Davidson, W. L. Phys. Rev.,1948, 74, 116-7.
- [2] Rosetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. J.Chem Phys., 1985, 82, 552.
- [3] Brus, L. J.Phys. Chem., 1986, 90,2555.
- [4] Henhlin, A. Chem. Rev., 1989, 89,89.
- [5] Wang, Y.; Herron, N. J. Phys. Chem., 1991, 95, 525.
- [6] Khairutdinov, R. F. Chemistry of semiconductor nanoparticles, Russian chemical reviews, 1998, 67 (2), 109-12.
- [7] Murugadoss, G.; Rajamannan, B.; Ramaswamy, V. Journal of Lumin, 2010, 130,2032-2039.
- [8] Norris, D. J.; Bawendi, M. G. Phys. Rev. B, 1996, 53, 16338.
- [9] Wang, L. W.; Zunger, A. J.Phys. Chem. B, 1998, 102, 6449.
- [10] YeChanghui; Fang Xiaosheng; Li Guanghai; Zhang LideAppl. Phys. Lett., 2004, 85, 15, 3035.
- [11] Chen, W.; Wang, Z.; Lin, Z.; Lin, L. Appl. Phys. Lett., 1997, 70,1466.
- [12] Bhargava, R. N.; Gallagher, D.; Hong, X.; Numikko, A. Phys. Rev. Lett., 1994, 72, 416.
- [13] Bhargava, R. N. J. Lumin, 1996, 70,85.
- [14] Brieler, F. J.; Froba, M.; Chen, L.; Klar, P. J.; Heimbrodt, W.; Krug Von Nidda, H. A.; Loidl, A. Chem. Eur. J., 2002, 81, 185.