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Biocompatible and water dispersible ZnS:Mn nanocrystals conjugated with L-methionine

Annie Sujatha.R¹*, Joseph Stalin.P², Muthamizhchelvan.C¹

¹Department of Physics and Nanotechnology,SRM University ²Department of Physics, Cauvery engineering College,Tiruchirapalli India

Abstract : Water dispersible ZnS:Mn nanocrystals were synthesized by capping the surface of the nanocrystals with the methionine. The aminoacids capped ZnS:Mn nanocrystal powders were characterized by XRD, HR-TEM, SEM and FTIR..The optical properties of the aminoacids capped ZnS:Mn colloidal nanocrystals were also measured by UV/Vis and solution photoluminescence (PL) spectroscopies in aqueous solvents. The XRD pattern of methionine capped ZnS:Mn nanoparticles correspond to hexagonal structure of ZnS . The FTIR analysis of the samples was performed and the functional groups assignments were made. UV-Visible spectrum of methionine capped ZnS:Mn shows that λ_{max} is observed at 243nm.This indicates that the absorption shifts towards shorter wavelength because of the particle size reduction. Photoluminescence spectrum of methionine capped nanoparticles shows the emission wavelength peaking at 390 nm .The surface morphological studies were performed through SEM and TEM studies. The formation of hexagonal shaped nanoparticles is clearly seen in the SEM micrograph. The size of the particles as seen from the SEM is around 2µm. TEM pictures show a particle size of 5-10 nm. The particles formed are homogenous as revealed in the TEM image.

Key words-Aminoacid, Photoluminescence, methionine, hexagonal.

Introduction

Zinc sulphide, one of the wide band gap II-VI semiconductors can be tuned for diverse applications starting from display devices to biological applications due to its ability of being doped with transition metal ions making it a promising phosphor material¹. Manganese doped zinc sulphide phosphors have become more significant owing to their excellent optical and magnetic properties². ZnS:Mn as fluorescent probes for biological applications requires it to be watersoluble which can be achieved by surface modifying them using sets a prerequisite that it has to be water soluble^{3,4,5}. This can be achieved by biologically modifying the surface of a semiconductor.

Water dispersible semiconductor nanocrystals applied in biomedical area are grown in hydrophobic media so that they are hardly compatible with biological systems^{6,7}. In addition, it was shown that the photoluminescence efficiency for the amino acid capped ZnS:Mn nanocrystals increased up several times after the surface modification. This phenomenon resulted from the additional energy transfer of surfactant to Mn^{2+} metal ion as well as reducing the energy loss due to non-radioactive transition by the surface modification.

Amino acid ligands such as histidine and cystein⁸ were developed as surface capping agents for undoped ZnS nanocrystals and were reported as effective capping ligands in the synthesis of narrow range size distributed nanocrystals, which is difficult to achieve in aqueous solution due to different dissociation constants for ZnS and MnS in water⁹. When manganese is incorporated in ZnS, the interaction between d electron states of manganese ion and sp electronic states of the host results in enhanced luminescence compared to the undoped zinc sulphide. Long luminescence time of the manganese doped ZnS nanocrystal has proved it to be an ideal candidate as biolabelling agent and display applications¹⁰.

Luminescent centers of Mn doped nanocrystal with higher transition rates has been reported earlier by Bhargava et al^{11,12}. In this paper synthesis and characterization of manganese doped zinc sulphide capped with L-aminoacid ligands Methionine are reported.

Materials and methods:

All the chemicals purchased were analytical grade and used without further purification. The preparation method was similar to that used for the synthesis of ZnS:Mn capped with arginine via complex formation. Zinc (II) methionine was formed as intermediate complexes in the reaction before the formation of the final product aminoacid capped ZnS:Mn.

The zinc aminoacid complex was prepared by taking 50 ml solution of $ZnSO_4 \cdot 5H_2O$ (2.88 g, 10 mmol) added to 20 mmols of L-Methionine (3.28 g) and NaOH (0.8 g, 20 mmol) kept in ice water bath. The solution was stirred for 1 hour and the resulting powder was dissolved in Tris buffer solution. To the complex formed a mixture of manganese sulphate MnSO₄·H₂O (0.02 g, 0.1 mmol) and Na₂S (0.40 g, 5 mmol) dissolved in a 20 mL of 0.01M HCl solution was added and allowed to stir for 1 hr. Ethanol was added resulting in yellow-white precipitations at the bottom of the flask centrifuged and the solids were dried in an oven

The structure of the product obtained was characterized by X-ray Diffractometer with CuK α radiation (λ =1.5406 Å), using X'per PRO (PANalytical) advanced with 2 θ ranging between 20° and 80° at the scanning rate of 0.025° per second. Optical absorption measurements were performed using Varian Cary 5E UV–Vis NIR spectrophotometer in the range of 200–800 nm. Photoluminescence spectrum for the obtained product was recorded using He–Cd Laser with the excitation wavelength of 325 nm. Morphology of the sample was studied using FEG field-emission scanning electron microscopy (FESEM) High resolution transmission electron microscope images were obtained by a TEM JEOL JEM 2100F at an accelerating voltage of 200 kV.

Results and Discussion

1. Structural determination-XRD studies

Fig. 1 shows the XRD pattern of methionine capped ZnS:Mn nanoparticles. The X-ray diffractogram with dspacings of 3.9, 3.3, 2.9, 2.8, 2.6, 2.4, 2.33, 1.9 Å correspond to hexagonal structure of ZnS (JCPDS N0.89-2423). The other peaks present in the diffractogram is consistent with the peaks of aminoacid. The narrow peaks are indication of the formation of smaller size of the particles. The average size of the crystallites is around 15-20 nm for the samples calculated using Debye-Scherrer formula.

 $D = 0.9\lambda / \beta \cos\theta$

Where Dis the mean particle size in nm, K is the geometric factor (0.94), λ is the X-ray wavelength (1.5406 Å), β is the halfwidth of diffraction peak and θ is the angle of the diffraction peak.



Fig. 1. Powder XRD pattern of Methionine capped ZnS:Mn nanoparticles

2. Functional group and elemental confirmation studies

The FT-IR analysis of the samples were performed and the functional groups are shown as in Fig. 2. The peaks and the corresponding assignments of the frequencies are given in Table 1. The FT-IR spectra exhibits strong bands appearing in 2970 cm⁻¹ and 2925 cm⁻¹ corresponding to CH_2 stretching vibrations. The peak assignments confirms the elements present in the synthesized product.



Fig. 2: FT-IR spectrum of methionine capped ZnS:Mn nanoparticles

Frequencies (cm ⁻¹) ZnS:Mn (Methionine)	Assigned functional groups of the zinc co-ordinated aminoacids		
1585, 1587	C-O stretching		
2110	C=O stretching		
1310	C-OH out of plane bending vibrations		
552	C-OH absorption		
2852	C-H stretching vibration		
2970	CH ₂ symmetric stretching vibrations		
2925	CH ₂ asymmetric stretching vibrations		
1385	CH ₃ scissoring vibration		
1615	Inplane bending of NH ₂ wagging mode		
622, 1041	ZnS vibrations		
3500-3400	Absorption due to hydroxyl groups		

Table 1:	FT-IR	assignment	for	ZnS:Mn ((Methionine))

3. UV-Vis absorption and bandgap plot

UV-Visible spectrum of methionine capped ZnS:Mn is shown in Fig. 3. In this spectrum λ_{max} is observed at 243 nm. This indicates that the absorption shifts towards shorter wavelength because of the particle size reduction. This spectrum shows that methionine capped ZnS exhibits significant blue shift. This is due to strong quantum confinement. The bandgap of the nanoparticles synthesized has been calculated as 5.18 eV using the Tauc plot of $E_g Vs (\alpha h \upsilon)^2$ as shown in Fig. 4. This reveals that when the size of the particles is very much reduced the energy state separation is too high ¹³.



Fig. 3: Optical spectra (UV-Visible absorption) of methionine capped ZnS:Mn nanoparticles



Fig. 4: Plot of hv Vs (ahv)² for methionine capped ZnS:Mn nanoparticles

4. Photoluminescence studies

Photoluminescence spectrum of methionine capped nanoparticles is shown in Fig. 5. The emission wavelength is peaking at 390 nm. This emission is due to the recombination of electron hole pair. The blue shift of the methionine capped ZnS:Mn nanoparticles demonstrates the strong quantum confinement. The absorption wavelength is observed at 243nm and the emission wavelength is observed at 390 nm which is highly blue shifted from that of the bulk material. This indicates the emission associated with the transition of electrons from trap state to conduction band ^{14, 15}.



Fig. 5: Optical spectra (Photoluminescence) of methionine capped ZnS:Mn nanoparticles

5. Surface Morphological studies

The surface morphological studies were performed from SEM and TEM studies. The formation of hexagonal shaped nanoparticles is clearly seen in the SEM micrograph Fig. 6. The image shows aggregation of the particles. The size of the particles as seen from the SEM is around 2 μ m. TEM pictures show a particle size of 5-10 nm. The particles formed are homogenous as revealed in the TEM image as shown in Fig. 7.



Fig. 6: SEM images of Methionine capped ZnS:Mn nanoparticles



Fig. 7: TEM images of methionine capped ZnS:Mn nanoparticles

Conclusion

Water soluble L-Methionine capped ZnS was prepared by wet chemical route by forming an intermediate complex. The structural investigation using XRD confirms the presence of the formation of the nanocrystals conjugated with L-methionine. The calculation of crystallite size from from Debye-Scherrer's formula is around 15-20nm. The photoluminescence spectrum shows emission peak at 390 nm and is attributed to the transition of electrons from trap state to conduction band. The FTIR peak assignments reveals the functional groups confirming the presence of elements in the formed product. From the UV visible spectrum it is observed that the maximum absorption peak occurs at 243 nm. Using Tauc plot the bandgap has been calculated to be 5.18 eV. Scanning electon microscopy studies shows a hexagonal shaped morphology. The particle size as calculated from the TEM images is around 5-10 nm. In summary water soluble L-aminoacid modified Zinc sulphide nanocrystals has been synthesized and its optical and structural characterization were performed making it suitable for biological applications.

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References

- 1. Fang, X.S., Bando, Y., and Golberg, D., Mater, J., Sci. Technol., 2008, 24; 512
- 2. Mattoussi, H., Mauro, J.M., Goldman, E.R., Green, T.M., Anderson, G.P., Sundar, V.C., Bawendi, M.G., Phys. Stat. Sol., 2001, 224,277
- 3. Lakowicz, J.R., Gryczynski, I., Gryczynski, Z., Nowaczyk, K., Murphy, C.J., Anal. Biochem., 2000, 280, 128
- 4. Mitchell, G.P., Mirkin, C.A., Letsinger, R.L., J. Am. Chem. Soc., 1999, 121,81221
- 5. Bruchez jr, M., Moronne, M., Gin, P., Weiss, S., Alivisatos, A.P., Science, 1998, 281, 2013
- 6. Crystal structure [online] available from http://wpcontent.answers.com/ wikipedia/commons/ thumb/ 5/5e/UnitCell.png/300px-UnitCell.png [Accessed 4 May 2009].
- 7. Eastoe, J., Fragneto, G., Robinson, B.H., Towey, T.F., Heenan, R.K., Leng, F.J., J. Chem. Soc. Faraday Trans., 1992, 88, 461.
- 8. Yi, G., Sun, B., Yang, F., Chen, D. J., Mater. Chem. 2001, 11,2928
- 9. Bernal, J.D., Kristallogr, Z., 1931, 78, 363
- 10. Simpson Jr, H.J., Marsh, R.E., Acta Cryst., 1966, 8, 550.
- 11. Bae, W., Mehra, R. K., Inorg. J., Biochem. 1998, 70, 125.
- 12. Bhargava, R. N., Gallagher, D., Phys. Rev. Lett. 1994, 72, 416
- 13. Thenneti Raghavalu., Ramesh Kumar G., Gokul Raj, S., Mathivanan, V., Mohan R. J., Crystal Growth., 2007, 307, 112.
- 14. Diem, M., Polavarapu, P.L., Oboodi, M., Nafie, L.A., J. Am. Chem. Soc., 1982, 104, 3329.
- 15. Godzisz, D., Czysym, M.H., Jesyszym, M.M., Spectrochim., Acta Part A 2003, 59(1), 681.