Core-shell Nanoparticles: Synthesis and Applications

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Abstract - **Core-shell nanoparticles are the unique class of nanoparticles. By changing the shell thickness we can change the properties of nanoparticles. In this paper we have reported the synthesis and applications of core-shell nanoparticles. Core-shell nanoparticles were synthesized by wet chemical precipitation method. The nanoparticles were stabilized by bio-compatible capping agent. Morphological characterization is done by XRD and TEM. Band gap measurements were done by UV-visible absorption spectra. The changes in optical and morphological properties were observed in case of capped and uncapped nanoparticles. Band gap increases with capping. Particle size was calculated by Brus equation. Particle size decreases with capping. These studies are very good for biological applications.**

Keywords - Core-shell, Bio-compatible.

1. INTRODUCTION

Semiconductor nanoparticles are one of the most challenging classes of new materials and constitute an active field of research. These materials have attracted much attention over the past few years because of their novel properties [Kumar et al., 2013, 2014; Singhal et al., 2012, 2013; Khan et al., 2011]. Most of the physical or chemical properties exhibited by these nanoparticles are due to their crystallites [A.P. Alivisatos 1996]. Further growth in their size is due to agglomeration of these crystallites to form primary particles. If this growth of particles is not controlled, then due to Ostwald ripening and Vander-Waals interactions between particles, they agglomerate and settle down.

This agglomeration can be arrested by either stabilizing them electro statically or by inducing steric hindrance at appropriate stages to achieve size selective synthesis during precipitation reaction [T.Kubo etal 2002; K.Manzoor etal 2004, H.C. Warad etal 2005; Gopa Ghosh etal 2006]. In order to control the growth one can use different organic and inorganic capping agents to passivate the free nanoparticles [Weon Bae etal 1997; C. Torres-Martyonez etal 1999]. L-Cysteine is a non-toxic material which contains ionisable carboxyl and amine groups, and this amino acid moiety imparts biofunctionality to the nanoparticles.

2. EXPERIMENTAL

The ZnS nanoparticles were synthesized by chemical precipitation method. Homogeneous solutions of zinc acetate and sodium sulphide were prepared in aqueous media. 0.5M $(Zn(CH_3COO)_2.H_2O)$ and 0.5 M Na_2S solutions were used for the synthesis of ZnS nanoparticles. L-Cysteine was also added as a capping agent to the reaction medium for controlling the particle size. First of all no capping agent has been used for the stabilization of the nucleated particles; instead, the nanoparticles are allowed to interact freely in the aqueous medium. In the second attempt L-Cysteine (2.0% at. wt) was added in 0.5 M zinc acetate and then 0.5 M sodium sulphide was added drop wise. The white precipitate appears soon after the addition of sodium sulphide (Na_2S). The stirring was allowed for 15 minutes at room temperature using a magnetic stirrer. Then the particles were centrifuged at 4000 rpm for 5 minutes. The precipitated particles were filtered using Whatman 40 filter paper. The particles were washed several times using double distilled water to remove the last traces of adhered impurities. The washed particles were dried at 60ºC in vacuum oven.

3. RESULTS AND DISCUSSION

crystal structure and three broad peaks corresponding to the (111), (220) and (311) planes. which appear at 2θ values of 28.5^0, 47.6^0 and 56.4^0 respectively. Broadening of XRD peaks shows the formation of nanocrystals of ZnS. Crystallite size of ZnS nanoparticles is calculated by Scherer's equation,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D-crystallite size (Å), λ (Å) =1.54 be the wavelength of Cu Kα radiation and β-corrected half width of the diffraction peak. The primary crystallites' size is around 2.10 nm for capped and 2.24 nm for uncapped nanostructures.
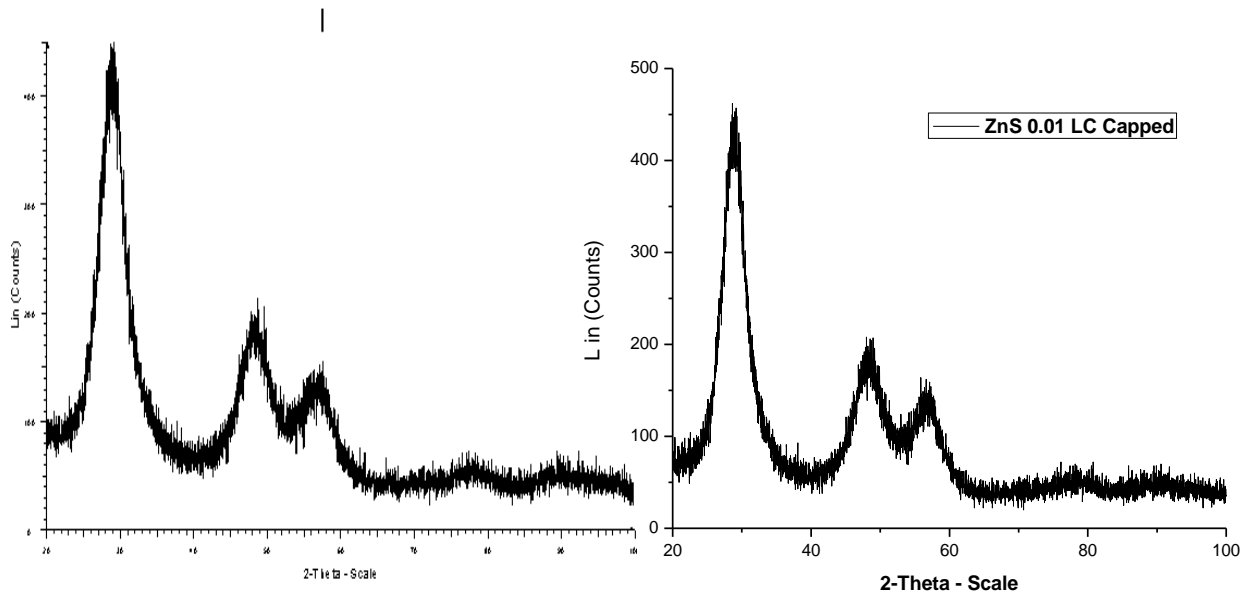

Figure1: XRD studies of uncapped ZnS and L-Cysteine capped ZnS

Figure2(a) & Figure2(b) shows the TEM of ZnS nanoparticles obtained in the absence and in presence of L-Cysteine.
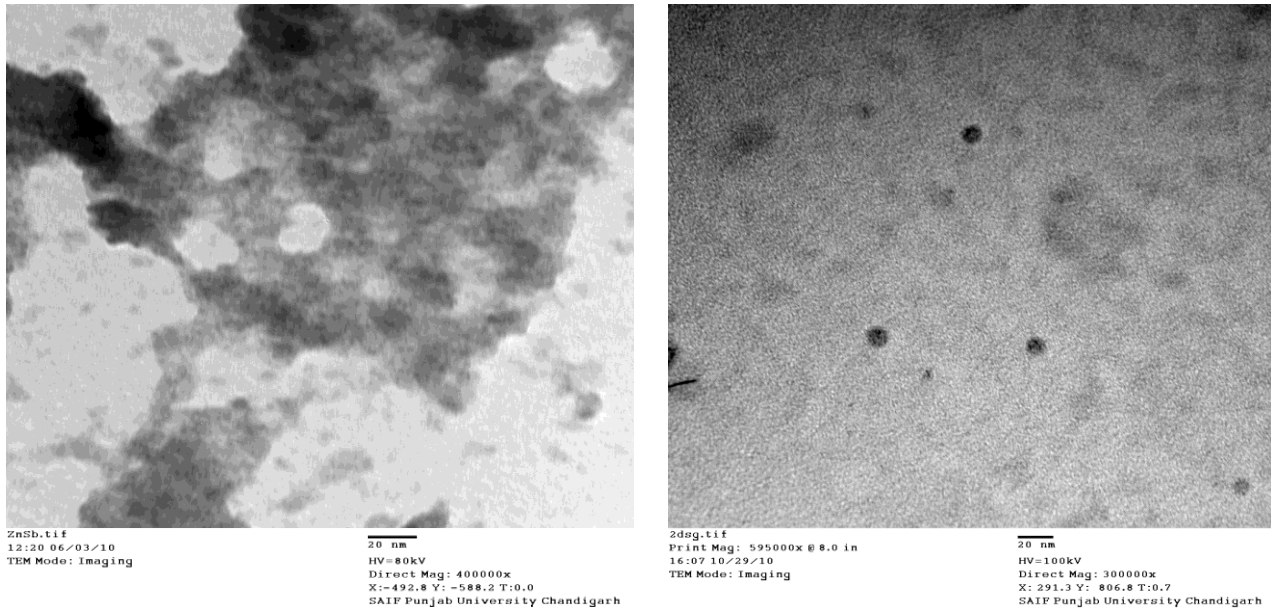
Figure2: TEM of (a) Uncapped ZnS nanoparticles (b) Uncapped ZnS nanoparticles

The figure indicates that the L-Cysteine capped ZnS nanoparticles are monodispersed in nature. Uncapped nanoparticles on the other hand are agglomerated. TEM studies confirm the formation of ZnS capped and uncapped quantum dots. Average particle as obtained from TEM studies is 2.5 nm, which is in accordance with XRD results.

Figure3 shows the absorption spectra of uncapped and L-Cysteine encapsulated ZnS nanoparticles. The absorption edges are 292 nm and 297 nm for uncapped and capped ZnS quantum dots respectively. For obtaining the absorption characteristic of the samples, at first the transmittance(T) at different wavelengths are measured using different values of absorbance and then absorption coefficient(α) at the corresponding wave- lengths are calculated using the Beer-Lambert's relation,

$$\alpha = (1/d) \ln(1/T) \qquad [1]$$

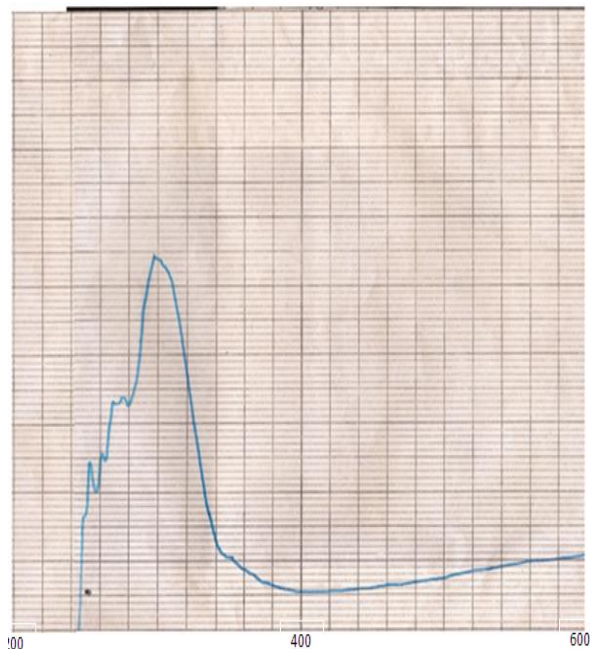Where d is the path length which is 1cm in this case.
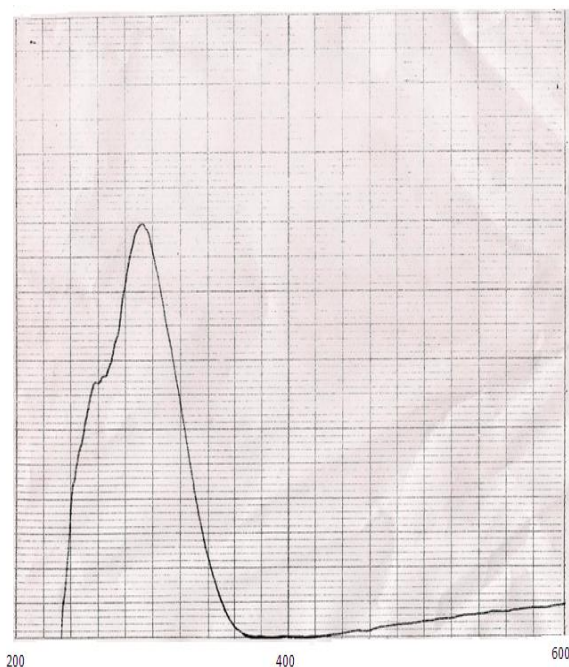
Figure3: UV-Visible Absorption spectra of (a) uncapped (b) capped ZnS quantum dots

The relation between the incident photon energy (hν) and the absorption coefficients (α) is given by the following relation, $(\alpha h\nu)^{1/m} = c (h\nu - E_g)$ where, c is a constant and E_g is the band gap of the material and the exponent m depends on the type of the transition.
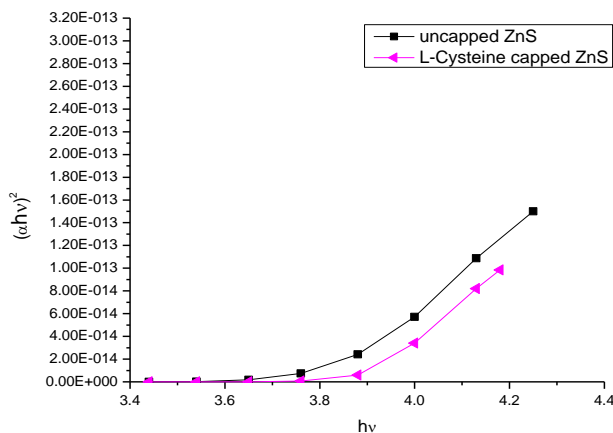

Figure4: Bandgap Comparison

For direct and allowed transition m = 1/2, in direct transition, m = 2, and for direct forbidden, m = 3/2.

For calculating the direct band gap value $(\alpha h\nu)^2$ versus hν is plotted as shown in Figure4 by extrapolating the straight portion of the graph on hν axis at α= 0, the optical band gaps are calculated and found to be 3.85 eV and 3.91 eV for uncapped capped ZnS quantum dots.

Further particle size of synthesized nanoparticles have been calculated by using Brus equation [L.E. Brus 1984] and found to be 2.72 nm and2.43 nm for uncapped and capped ZnS nanoparticles. The results of UV-studies are also in accordance with XRD and TEM studies. Hence it is clear that bandgap of ZnS increases and particle size decreases with capping.

4. CONCLUSIONS

Core-shell ZnS quantum dots have been synthesized by chemical precipitation method. Optical and morphological measurements have been carried out to investigate effect of capping on ZnS nanoparticles. XRD results show the crystallite size to be 2.10 nm for capped and 2.24 nm for uncapped ZnS depending upon the peaks. From UV-visible studies it is clear that the band gap increases with capping. As L-Cysteine is a bio-compatible capping agent so we can use L-Cysteine capped ZnS quantum dots for biological applications.

REFERENCES

[1] A.P. Alivisatos (1996). *The Journal of Chemical Physics*. 100, 13226-13239.

[2] C. Torres-Martyonez, L. Nguyen, R. Kho, W. Bae, K. Bozhilov, V. Klimov and R.K. Mehra (1999). *Nanotechnology*. 10, 340–354.

[3] D. Denzier, M. Olschewski, and K. Sattler (1998). *Journal of Applied Physics*. 2841-2845.

[4] Dongjin Kima, Ki-Deuk Min, Jongwon Lee, Jeong Ho Park and Jong Han Chun (2006). *Materials Science and Engineering B*. 131 13–13117.

[5] Gopa Ghosh, Milan Kanti Naskar, Amitava Patra and Minati Chatterjee (2006). *Optical Materials*. 28, 1047–1053.

[6] H.C. Warad, S.C. Ghosh, B. Hemtanon, C. Thanachayanont and J. Dutta (2005).*Science and Technology of Advanced Materials*. 6, 296–301.

[7] K.Manzoor, S. R Vadera, N. Kumar, and T. R. N. Kutty(2004). *Solid State Communications* .129, 469-473.

[8] Khan, P. Y., Singhal, M., Sharma, J. K., Lu, C. H., & Kumar, S. (2011). UV-visible Absorbtion Studies of ZnSe Chalcogenide Quantum Dots. *Nonlinear Optics*, *42*(1).

[9] Kuldeep S. Rathore, D. Patidar, Y. Janu, N.S. Saxena, Kananbala Sharma and T. P.Sharma June(2008). *Chalcogenide Letters*. 5, 105 – 110.

[10] Kumar, S., Kang, T. W., Khan, P. Y., Kumar, S., Goyal, M., & Choubey, R. K. (2014). Study of electroless template synthesized ZnSe nanowires and its characterization. *Journal of Materials Science: Materials in Electronics*, *25*(2), 957-961.

[11] Kumar, S., Singhal, M., & Sharma, J. K. (2013). Functionalization and characterization of ZnS quantum dots using biocompatible l-cysteine. *Journal of Materials Science: Materials in Electronics*, *24*(10), 3875-3880.

[12] L.E. Brus (1984). Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. *The Journal of Chemical Physics*, 80, 4403 -4408.

[13] S. Wageh, Liu Shu-Mana, Fang Tian Youa and Xu Xu-Ronga(2003). *Journal of Luminescence*. 102–103, 768–777.

[14] Singhal, M., Sharma, J. K., & Kumar, S. (2012). Effect of biocompatible glutathione capping on core–shell ZnS quantum dots. *Journal of Materials Science: Materials in Electronics*, *23*(7), 1387-1392

[15] Singhal, M., Sharma, J. K., & Kumar, S. (2013). Morphological and Optical Behaviour of Pyridine Capped Bio-Compatible ZnS Quantum Dots. *Advanced Science, Engineering and Medicine*, *5*(2), 133-139.

[16] T.Kubo, T. Isobe, and M. Senna (2002). *Journal of Luminiscence*. 99, 39-45.

[17] Weon Bae, Rizwana Abdullah, David Henderson, and Rajesh K. Mehra (1997). *Biochemical and Biophysical Research Communications*. 237, 16–23.