Synthesis, surface characterization and optical properties of 3-thiopropionic acid capped ZnS:Cu nanocrystals

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Abstract. 3-Thiopropionic acid (TPA) capped ZnS:Cu nanocrystals have been successfully synthesized by simple aqueous method. Powder X-ray diffraction (XRD) studies revealed the particle size to be 4·2 nm. Surface characterization of the nanocrystals by FTIR spectroscopy has been done and the structure for surface bound TPA based on spectral analysis was proposed. The optical studies were done using UV-VIS spectroscopy and particle size and diameter polydispersity index (DPI) were calculated. Photoluminescence (PL) spectrum reveals emission related to the transition from conduction band of ZnS to t_2 level of Cu^{2+}. Electron microscopy was also done by scanning electron microscopy (SEM).

Keywords. ZnS:Cu nanocrystals; 3-thiopropionic acid; diameter polydispersity index; photoluminescence; powdered XRD; electron microscopy.

1. Introduction

Nanoscience and nanotechnology conjures up visions of making, imaging, manipulating and utilizing materials that are really small (Pradeep 2007). Semiconductor nanosized and quantum confined materials are now poised to revolutionize the electronic, chemical, biotechnology and biomedical fields (Havanscak 2003; Larson *et al* 2003; Daniel and Astruc 2004; Sapra *et al* 2005). Functionalization of surface is one of the most important aspects of nanoparticles fabrication (Jun *et al* 2006). Doped ZnS semiconductor materials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, and optical sensors. Accordingly, study of luminescence properties of ZnS has received special attention. The bulk ZnS peak is expected at 338 nm (3·67 eV). Many of the ZnS systems were made using complicated methods with organic solvents, which were not suitable for bioimaging applications (Zhang and Li 2004; Kuzuya *et al* 2005; Ehlert *et al* 2008). With the decrease of particle size extremely particle high surface to volume ratio causes the surface states to act as luminescence quenching centres. Hence, the passivation of surface is of crucial importance for the application of luminescent semiconductors (Panda and Chaudhuri 2007). Surfactants play an important role in the control of dispersed particle sizes, optical properties and suitability by passivating surface of the nanocrystal (Chan and Nie 1998). 3-Thiopropionic acid, also named as β-mercaptopropionic acid, contains two functional groups, thiol and carboxylic acid which can be deprotonated allowing it to bind to surface of the nanoparticles. Doped ZnS nanocrystals can be considered for fluorescence biolabelling agent due to its long luminescence lifetime (Suyver *et al* 2001) and no elemental toxicity. Here, we present the synthesis of thiopropionic acid capped ZnS:Cu nanocrystals by simple aqueous method that avoids the detrimental organometallic precursors and high temperature. The obtained nanocrystals were characterized for their morphology and structure. The optical properties were also investigated.

2. Experimental

2.1 *Materials and methods*

A.R. grade zinc acetate dihydrate, copper acetate monohydrate, sodium sulphide nonahydrate, mercaptopropionic acid (TPA), ethanol etc were obtained commercially and used without further purification. Double distilled water was used for all sample preparation and dilution process. In the present procedure 3·5 ml of 3-thiopropionic acid was dissolved in 36 ml of D/D water and stirred for 5 min. While stirring continuously, 5 ml of 1 M zinc acetate solution as also the required amount of copper acetate solution was added drop wise to the above solution. The molar concentration of Cu^{2+} to Zn^{2+} was fixed at 0·1%. pH of the solution was adjusted to 12 with 2N NaOH. The above mixture was stirred for 10 min. Then 5 ml of 1 M sodium solution was added to this mixture drop wise. After 5 min 15 ml of 1 M zinc acetate solution was again added to the above solution. A transparent solution was

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obtained. To obtain powdered nanocrystals, cold ethanol precipitation was done, the precipitate was isolated by centrifugation, washed several times with ethanol to remove adhered impurities and finally dried in an oven at 60°C.
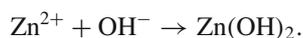
The prepared sample was characterized by powder XRD using Rigaku Miniflex with Cu Kα (1·5406 Å) radiation in a 2θ range of 20°–70° at a step size of 0·02° (2θ). The FTIR spectrum was recorded on SHIMADZU FTIR 8400S spectrophotometer. UV-VIS spectra was recorded on a Systronic UV spectrophotometer 119. The scanning electron microscopy (SEM) measurements were recorded on a FEI Quanta 200 microscope equipped with an EDX unit. The PL of the as prepared nanoparticles was recorded at room temperature using SHIMADZU RF 5301 PC Spectrofluorophotometer.
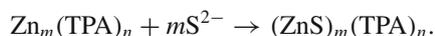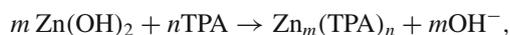
3. Results and discussion

3.1 *Reaction mechanism*

The following mechanism is proposed for the synthesis of TPA capped ZnS:Cu nanocrystals.

At pH $6·5 - 8$,

$$Zn^{2+} + OH^- \rightarrow Zn(OH)_2.$$

At pH > 9,

$$m\,Zn(OH)_2 + nTPA \rightarrow Zn_m(TPA)_n + mOH^-,$$

$$Zn_m(TPA)_n + mS^{2-} \rightarrow (ZnS)_m(TPA)_n.$$

At slightly alkaline condition, Zn^{2+} ion reacts with OH^- to form zinc hydroxide. Under more basic concentration, $Zn(OH)_2$ forms complex through chelating interactions of carboxyl and dissociated thiol. When Na_2S is introduced, S^{2-} may destroy the complex and combine with Zn^{2+} due to strong interaction than those between Zn^{2+} and deprotonated TPA (Crisponi *et al* 2002). Residual thiopropionic chelated complex may be adsorbed on the surface of growing ZnS nuclei and form a denser covering layer which may block further particle growth.

The solubility of CuS is less than that of ZnS hence, it seems that Zn^{2+} and Cu^{2+} cannot be coprecipitated with S^{2-} ions but thiol group present in the thiopropionic acid minimizes the solubility difference between CuS and ZnS by coordinating with Cu^{2+} and thus the possibility of coprecipitation of ZnS and CuS can be greatly improved during the synthesis and this makes it possible to obtain ZnS:Cu nanoparticles in which Cu^{2+} ions replace the Zn^{2+} ions in the lattice.

3.2 *Grain size studies*

Figure 1 shows the measured XRD pattern of ZnS:Cu – TPA. Three broad peaks corresponding to the (111), (220) and (311) planes were observed. Crystallite size of capped
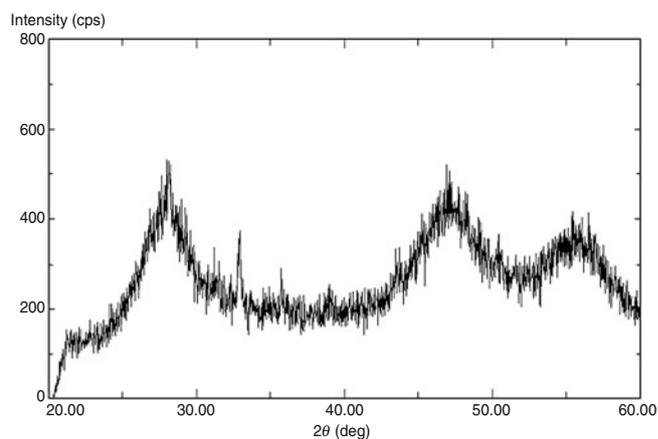
Figure 1. XRD diffraction pattern of TPA capped ZnS:Cu nanocrystals.
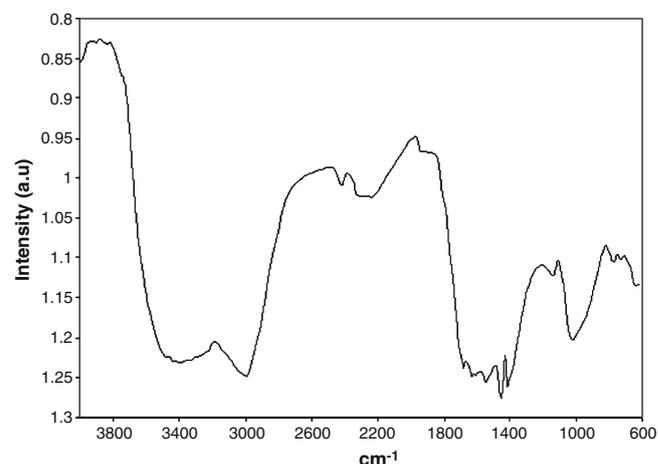
Figure 2. FTIR spectrum of TPA capped ZnS:Cu nanocrystals.

ZnS:Cu was calculated by following Scherrer's equation (Guinier 1963)

$$D = K\lambda/\beta \cos\theta.$$

The average size calculated from the above formula is 4·2 nm. The broadening of the XRD peak indicated the formation of ZnS nanocrystals.

3.3 *FTIR spectra*

The form of the 3-TPA adsorbed on the ZnS:Cu nanoparticles is inferred from FTIR spectra as shown in figure 2. The broad feature between 3000 and 3500 cm^{-1} is due to O–H stretching of carboxylic group. The peak at 1414 cm^{-1} is due to bending vibration of methylene groups in thiopropionic acid while the peak at 2914 cm^{-1} is due to CH$_2$ stretching mode of TPA. The C–O stretching vibration is observed

between 1016 and 1103 cm^{-1}. Due to deprotonation of carboxylic acid group the C=O stretching band of neat TPA is switched to an antisymmetric OCO stretch, 1630 cm^{-1}. The O–H bend is observed at 1451 cm^{-1}. The absence of S–H stretch at 2554 cm^{-1} suggests that TPA exists as thiolate on the nanocrystals surface.

3.4 *Optical absorption studies*

Absorption spectrum of TPA capped ZnS:Cu nanoparticles have been studied by dispersing 0·001g of the sample in 1ml of water as shown in figure 3. The spectrum reveals that the intensity increases toward shorter wavelength and attains a maximum at 290 nm. It can be seen that a broad absorption peak is obtained which may be attributed to the formation of nanoaggregates of the nanoparticles as can be seen from the SEM image. The doping of Cu^{2+} does not change the bandgap significantly due to very little concentration since the particle size does not change appreciably but can drastically change the luminescent properties. Optical excitation of electrons across the bandgap is strongly allowed transition thus it causes an abrupt increase in the absorptivity at wavelength corresponding to gap energy. Blue shifting of absorption peak (bulk 345 nm) is due to quantum confinement of the excitons present in the sample resulting in more discrete energy of the spectrum of individual nanoparticles. The
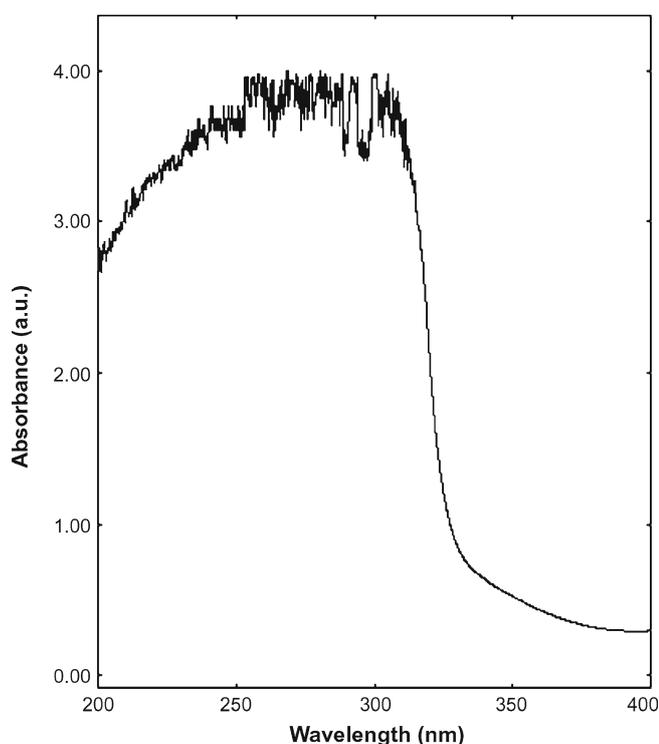
average particle size present in the nanocolloid can be determined by using the mathematical model of effective mass approximation (Brus 1986). The following equation derived, describes the particle size (r, radius) as a function of peak absorbance wavelength (λ_p) for ZnS nanocrystals.

$$r \text{ (nm)} = \left\{ -0{\cdot}2963 + \sqrt{(-40{\cdot}1970 + 13620/\lambda_p)} \right\} \Big/ \left\{ -7{\cdot}34 + 2481{\cdot}6/\lambda_p \right\}.$$

The particle size obtained is 3·8 nm for TPA capped ZnS nanoparticles, which is consistent with the value obtained by Scherrer's formula.

3.5 *Diameter polydispersity index (DPI)*

Width of the particle size distribution can be related to $d_{1/2}$ value which is given by the difference between the particle diameter calculated from the edge of the absorption and the particle diameter calculated from the position of exciton shoulder, λ_e. Assuming a gaussian distribution it is possible to convert $d_{1/2}$ into a diameter polydispersity index (DPI) (Moffit *et al* 1995) according to the following formula

$$\text{DPI} = \left(\sigma_d / d_s \right)^2 + 1,$$

where σ_d is the standard deviation taken as half of $d_{1/2}$ and d_s the mean particle diameter which corresponds to position of exciton shoulder. Taking into account that DPI = 1 defines a monodispersed sample, the calculated value of DPI implies a relatively low size of polydispersity of ZnS nanoparticles. The calculation of DPI is shown in table 1.

3.6 *Electron microscopy*

The microstructure of the nanocrystals has been examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis of the prepared nanocrystals is shown in figures 4 (a), (b) and (c), respectively.

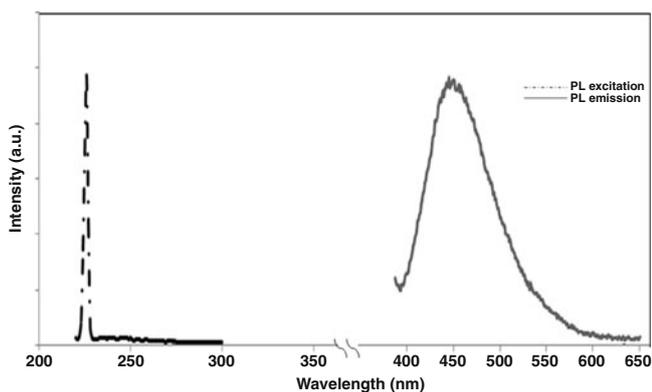### 3.7 *PL spectrum of TPA capped ZnS:Cu nanoparticles*

Figure 5 shows the room temperature PL excitation and emission spectra of TPA capped ZnS:Cu nanoparticles. The excitation peak was obtained at around 240 nm. The

Figure 3. Absorption spectrum of TPA capped ZnS:Cu nanocrystals.

Table 1. Diameter polydispersity index for TPA capped ZnS:Cu.

λ_e	λ_p	d_e	d_p	$d_{1/2}$	DPI
313 nm	290 nm	5·1 nm	3·8 nm	1·3 nm	1·02
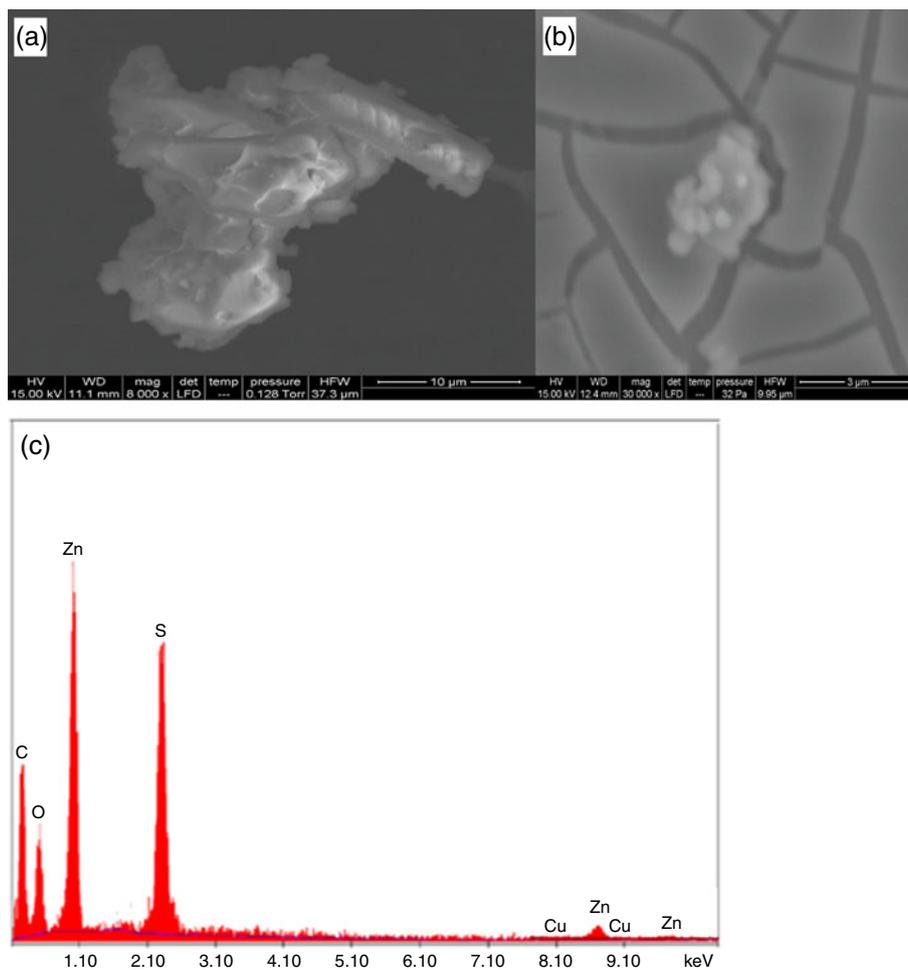
Figure 4. (**a**), (**b**) SEM images of TPA capped ZnS nanocrystals and (**c**) EDX spectrum of TPA capped ZnS:Cu nanocrystals.

Figure 5. PL spectrum of TPA capped ZnS:Cu nanocrystals.

incorporation of Cu^{2+} in the ZnS host can be confirmed from the fact that undoped ZnS shows an emission at around 424 nm (Warad *et al* 2005) resulting from the transition of electrons from the shallow states near the conduction band to sulphur vacancies present near the valence band. In the present study, blue emission at about 460 nm is attributed to the transition between conduction band of ZnS host and the acceptor like $t_2(d^9)$ state of Cu (Manzoor *et al* 2004; Corrado *et al* 2010).

4. Conclusions

In this paper we have reported the synthesis of TPA capped ZnS:Cu nanoparticles by simple aqueous method. Optical studies revealed that the nanoparticles formed were monodispersed (DPI $\sim$ 1). The PL spectrum shows a broad emission peak at around 460 nm. Doping Cu^{2+} in the ZnS nanoparticles causes a red-shift in the emission peak.

Acknowledgement

References

Brus L E 1986 *J. Phys. Chem.* **90** 2555

Chan W C W and Nie S 1998 *Science* **281** 2016

Corrado C, Hawker M, Livingston G, Medling S, Bridges F and Zhang J Z 2010 *Nanoscale* **2** 1213

Crisponi D *et al* 2002 *Polyhedron* **21** 1319

Daniel M C and Astruc D 2004 *Chem. Rev.* **104** 293

Ehlert O, Bucking W, Riegler J, Merculov A and Nann T 2008 *Microchim. Acta* **160** 35

Guinier A 1963 *X-ray diffraction* (San Francisco: W H Freeman)

Havanscak K 2003 *Mater. Sci. Forum* **415–416** 85

Jun Y W, Jang J T and Cheon J W 2006 *Bull. Korean Chem. Soc.* **27** 961

Kuzuya T, Tai Y, Yamamuro S and Sumiyama K 2005 *Sci. Technol. Adv. Mater.* **6** 84

Larson D R *et al* 2003 *Science* **300** 1434

Manzoor K, Vadera S R, Kumar N and Kutty T R N 2004 *Solid State Commun.* **129** 469

Moffit M, McMahon L, Pessel V and Eisenberg A 1995 *Chem. Mater.* **7** 1185

Panda S K and Chaudhuri S 2007 *J. Coll. Interf. Sci.* **313** 338

Pradeep T 2007 *Nano: the essentials* (USA: Tata Mc Graw Hill) p. 1

Sapra S, Prakash A, Ghangrekar A, Periasamy N and Sarma D D 2005 *J. Phys. Chem.* **B109** 1663

Suyver J F, Wuister S F, Kelly J J and Meijernik A 2001 *Nano. Lett.* **1** 429

Warad H C, Ghosh S C, Hemtanon B, Thanachayanont C and Dutta J 2005 *Sci. Technol. Adv. Mater.* **6** 296

Zhang Y and Li Y D 2004 *J. Phys. Chem.* **B108** 17805