

Cu²⁺ and Mn²⁺ Doped ZnS Nanoparticles: Synthesis and Optical Characterization

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ABSTRACT

Semiconductor fluorescence nanoparticles have become promising alternative to organic fluorophores owing to their tunable fluorescence and high resistance to photobleaching. Currently, many of the available semiconductor fluorescence nanoparticles are inherently insoluble and or highly carcinogenic to living systems. Therefore, the investigation of fluorescence ZnS nanoparticles (ZnS NPs) with possibility of modifying the surface and optical properties through ligand and doping respectively is apt to hydrophilic and biocompatible fluorescence nanoparticles. Herein, fluorescence ZnS NPs were prepared by colloidal synthetic route using Zn (NO₃)₂·6H₂O, Na₂S and mercaptopropionic acid (MPA) ligand as precursors at ambient and basic pH. The influence of Cu²⁺ and Mn²⁺ as dopants on the fluorescence property of ZnS was evaluated. The as-prepared nanoparticles showed blue and pale green fluorescence colour and were further optically characterized using UV-Visible spectroscopy (UV-Vis) and fourier transform infrared (FT-IR) spectroscopy. UV-visible spectra of the ZnS NPs showed absorption maxima corresponding to blue shift in comparison with the bulk indicative of nano-sizing. FT-IR revealed bands corresponding to hydrophilic groups (O-H_{str}, C=O_{str}, and C-O_{str}) which enhanced their dispersibility in aqueous solution and also confirming effective interaction between the ligand and the NPs. Overall, the results herein suggest that the nanoparticles can be explored as potential materials for bioimaging application.

Keywords: Dopants, mercaptopropionic acid, Nanoparticles, UV-Vis, ZnS

INTRODUCTION

Nanomaterials which are of relevance in nanoscience and applied in nanotechnology have at least one of their dimensions within the range of 1-100 nm [1]. Specifically, semiconductor nanoparticles with physical dimensions ranging from 1-10 nm (quantum dots) have become promising alternatives to organic fluorophores. At this dimension, they possess size and

composition tunable optical and electronic properties due to quantum confinement effects [2]. Their high resistance to photobleaching makes them superior over the traditionally used organic fluorophores. However, many of the useful semiconductor nanoparticles are of highly toxic materials such as CdTe [3] and PbS [4], furthermore, establishing surface hydrophilicity involves long-reaction time and multistep procedures [5-6].

Zinc sulphide (ZnS) is a semiconductor with a wide direct band gap of 3.68 eV at room temperature [7]. Its optical properties can be tuned by doping. Although, fluorescence ZnS nanoparticles (ZnS NPs) is a benign replacement for cadmium-based quantum dots, which are known to be highly carcinogenic to living systems [8], including other inherently toxic metal chalcogenide/salt-based NPs. Nevertheless, its surface requires modification to enhance solubility, stability, and biocompatibility to facilitate its suitability as candidate for bioimaging or diagnostic agent since a great deal of physiological natural macromolecules exists in water-based environment.

Several pathways via the ‘bottom up’ methodologies involving sol-gel [9], microwave irradiation [10] and colloidal synthesis [11] have been developed to synthesize ZnS nanoparticles using various capping agents (ligands) for surface modification. Hitherto, obtaining a monodisperse ZnS nanoparticles with good fluorescence in a single facile step has been a major concern.

Herein, we report the colloidal synthesis of hydrophilic fluorescence ZnS NPs at ambient temperature with Zn(NO₃)₂·6H₂O, Na₂S and MPA (ligand) precursors as a simple, low-cost strategy.

MATERIALS AND METHODS

Materials

MPA (Mercaptopropionic acid), Zn(NO₃)₂·6H₂O and Na₂S. Other reagents include NaOH (Sigma-Aldrich), NH₄OH, CuCl₂, MnCl₂, and distilled water.

Colloidal Synthesis of ZnS NPs

Hydrophilic fluorescence zinc sulphide nanoparticles was synthesized in acidic medium (pH 5) at ambient temperature (25°C) by reacting Zn(NO₃)₂·6H₂O and Na₂S precursors according to the method described by Li et al [12] with modification. In a typical procedure, MPA solution (0.1 M, 4 mL) was added to aqueous solution of Zn(NO₃)₂·6H₂O (0.1 M, 1 mL) in a 100 mL

volumetric flask. The mixture was gently swirl followed by dropwise addition of aqueous solution of Na₂S (0.1 M, 1 mL). The resulting white colloidal solution was filtered.

The reaction was also carried out in basic medium (pH 12) through similar process described above with aqueous solution of NH₄OH (0.3 M, 10 mL) as solvent. The pH of the solution was adjusted with 5 M NaOH.

Colloidal Synthesis Synthesis of Doped ZnS NPs

Cu and Mn doped Zinc sulphide nanoparticles were synthesized in basic medium at room temperature. Typically, aqueous solution of Zn(NO₃)₂·6H₂O (0.1 M, 0.8 mL), CuCl₂ (0.1 M, 0.2 mL) and MPA solution (0.1 M, 4 mL) were added to aqueous solution of NH₄OH (0.3 M, 10 mL) in a 100 mL volumetric flask. The mixture was treated with Na₂S (0.1 M, 1 mL) as reported for the undoped reaction above to give Cu doped ZnS NPs. The reaction was carried out in a similar protocol with MnCl₂ to obtain the Mn doped ZnS NPs.

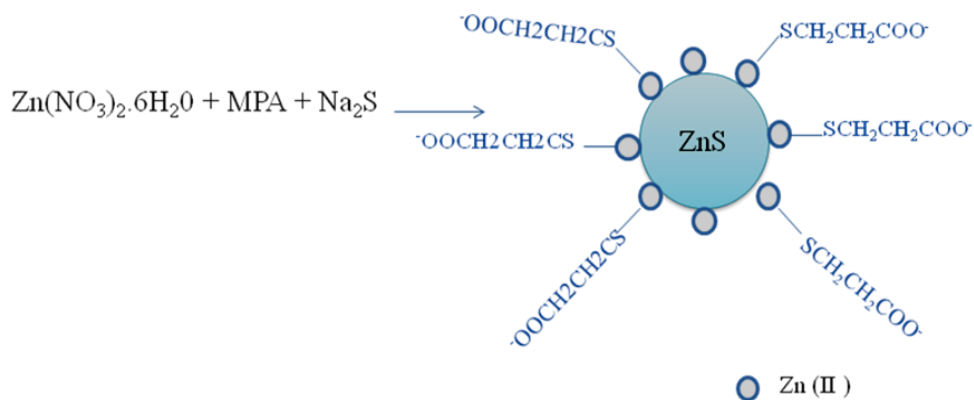
Optical Characterization

The optical properties of the prepared NPs were investigated variously by irradiation with 365 nm UV lamp, FT-IR and UV-Vis spectrophotometer. FT-IR infrared spectroscopy using BRUKER (vector 22) spectrophotometer over the range of approximately 4000-400 cm⁻¹ was used to determine the surface functional groups. UV-Vis absorption study were conducted on a T80⁺ UV-Vis spectrophotometer in the range 200 – 900 nm using distilled water and ammonium hydroxide for base line correction for reaction in acidic and basic medium reactions respectively. The band gap of the semiconductor was calculated to complement the UV-Vis study.

RESULTS AND DISCUSSION

Synthesis of Fluorescence ZnS NPs

Hydrophilic fluorescence ZnS NPs with MPA capping were obtained as shown in Scheme 1. During synthesis, upon the addition of the MPA ligand to Zn²⁺ precursor solution, Zn-MPA intermediate complex was initially formed which was then gradually used up with the dropwise addition of S²⁻ precursor solution to give the product. Thus, the product is proposed to consist of a zinc sulphide core surrounded by Zn-MPA shell (Scheme 1).



Scheme 1: ZnS core surrounded by Zn-MPA capping

Fluorescence Study

Fluorescence properties of the synthesized undoped and doped ZnS NPs with MPA capping investigated by irradiation with 365 nm hand held UV light are presented in Figure 1 (a-e). Bright blue fluorescence was observed only at high pH (pH 12). This suggests that the emission property of the ZnS NPs depends on the pH at which the synthesis was carried out for the undoped NPs. MPA is a bifunctional ligand containing both carboxylic and thiol groups which has different dissociation pH. The observed pH of synthesis-dependent fluorescence enhancement may probably be associated with increased dissociation of the carboxylic acid group including the deprotonation of the thiol group (-SH) of the MPA capping in solution at pH above the pK_a of free MPA (-COOH, dissociation constant (pK_a) = 4.34; -SH, pK_a = 10.20 [13]. This resulted in increased fluorescence intensity of the NPs as reprotonation which facilitates precipitation was low. Consequently, the pH was adopted for the synthesis of the doped ZnS NPs.

The presence of Cu²⁺ and Mn²⁺ as dopants resulted in pale green fluorescence. The dopants were perceived to introduce new energy levels within the band gap, thereby, modifying the photophysical property of the ZnS NPs. ZnS, being a wide direct band gap semiconductor material at room temperature could host dopants in form of impurities within its lattice structure which modifies its optical property. Cu²⁺ and Mn²⁺ are transition metals with [Ar] 3d⁹ and [Ar] 3d⁵ electronic configurations respectively. Both metal ions have similar ionic radii with Zn²⁺ and also contains free electrons in the d-orbitals. During synthesis, the metal ions replace some Zn²⁺ ions in the ZnS lattice creating defects. The extra electrons from the dopant ions are easily promoted to the conduction band through the absorption of light of lower energy which are

emitted as light of longer wavelength as evident from the perceived pale green colour when the electrons recombine with the holes. Tuning the emission colour or intensity of ZnS NPs makes it suitable candidate as diagnostic agent. The emission of highly intensified blue colour or green colour could presumably prevent spectra interference when used as diagnostic agent.

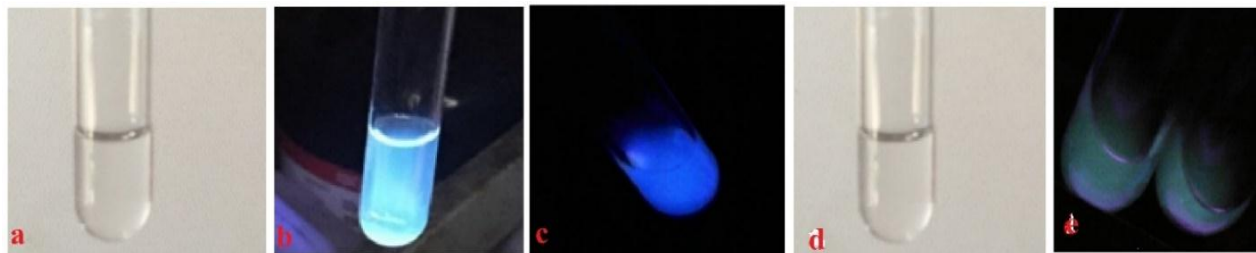


Figure 1:MPA capped undoped ZnS NPs (a) under normal light (b) Under 365nm light in acidic medium (pH 5) (c) Under 365nm light in basic medium (pH 12) (d) Cu doped MPA capped ZnS NPs under normal light (e) Cu doped (left) and Mn doped (right) MPA capped ZnS NPs under 365 nm light.

Fourier Infrared Spectroscopy (FT-IR) of ZnS NPs

FT-IR spectroscopy was used to probe the interaction between the MPA capping ligand and the nanoparticles. The spectra of MPA and MPA-capped ZnS NPs are shown in Figure 2 and notable assignment are presented in Table 1. The spectrum of MPA-capped ZnS NPs revealed shift in bands, significantly, reduction in C=O *str* relative to the MPA ligand (Table 1). The observed shift in bands in the spectrum of MPA-ZnS NPs from 3027 cm⁻¹ to 3019 cm⁻¹, 1701cm⁻¹ to 1688 cm⁻¹ and 1247 cm⁻¹ to 1275cm⁻¹ for O-H *str* ; C=O *str* and C-O *str* respectively are indicative of effective ligand-nanoparticles interactions. This presumably resulted from the coordination of Zn²⁺ to the deprotonated carboxylic acid (carboxylate) which lowers the C=O stretching frequency and also moved the C-O stretching to higher frequency. Additionally, the identified hydrophilic functional groups such as the –OH group on the surface of ZnS NPs enhances their dispersibility in aqueous medium.

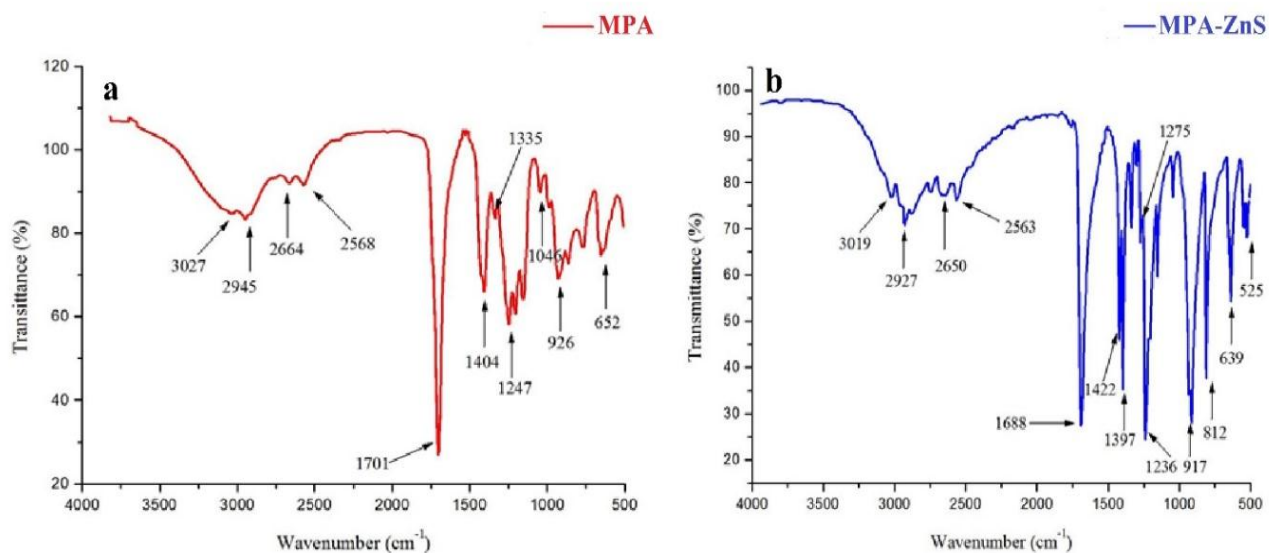


Figure 2 : FT-IR spectrum of (a) MPA (b) ZnS NPswith MPA capping

Table 1: Assignment of Infra red bands in MPA Capped ZnS

S/N	Present Study (cm ⁻¹)		Previous study (cm ⁻¹)	Assignment
	MPA	MPA- ZnS		
1.	3027	3019	3030 [8]	O-H _{Str} of carboxylic acid
2.	2945	2927	2934	C-H _{Asym str} of methylene
3.	2568	2563		S-H _{Str} of mercaptans
4.	1701	1688	1700, 1561[14]	C=O _{Str} of carboxylic acid
5.	1404	1422		C-H _{Bend} of methylene
6.	1335	1397		O-H _{Bend (in-plane)}
7.	1247	1275		C-O _{Str} of carboxylic acid
8.	926	917		O-H _{Bend (out of plane)} of carboxylic acid
9.	652	639		C-S _{Str}
10.	-	525		C-Zn _{Str}

UV-Vis Spectra of ZnS NPs

The absorption spectrum of hydrophilic fluorescence ZnS NPs is shown in Figure 3. Zinc sulphide NPs absorbs in the UV region (200-335 nm) of the spectrum [15], owing to the large energy gap between the conduction and valence band which brings the electronic transition energy within the high energy ultraviolet range. The absorption peak of ZnS NPs is centered at 323 nm with a tail spreading to the visible region in a characteristic pattern for the NPs. Cu and Mn doped MPA capped ZnS NPs showed absorption peaks at 243 nm. The observed peaks for the synthesized NPs are blue shifted relative to bulk ZnS which absorbs at 340 nm [16]. The observed blue shift of the absorption edges of the nanoparticles results from quantum confinement effect which suggest that the synthesized doped and undoped ZnS are nanosized.

Band gap values (Table 2) were calculated from UV-Vis absorption spectra using Equation 1. Where E is the band gap energy in eV, h is planck constant, c is the speed of light and λ is the wavelength.

$$\text{Band gap energy (E)} = hc/\lambda \quad (1)$$

Bulk Zinc have band gap of 3.68 eV at room temperature. The sizes shown in Table 2 were calculated using equation 2 as described by Ayodhya et al [7].

$$\text{Diameter (E)} = 0.32 - 2.9\sqrt{Eg} - 3.49/(3.50 - Eg) \quad (2)$$

Where, Eg is the band gap in eV and E, the diameter of NPs in nm.

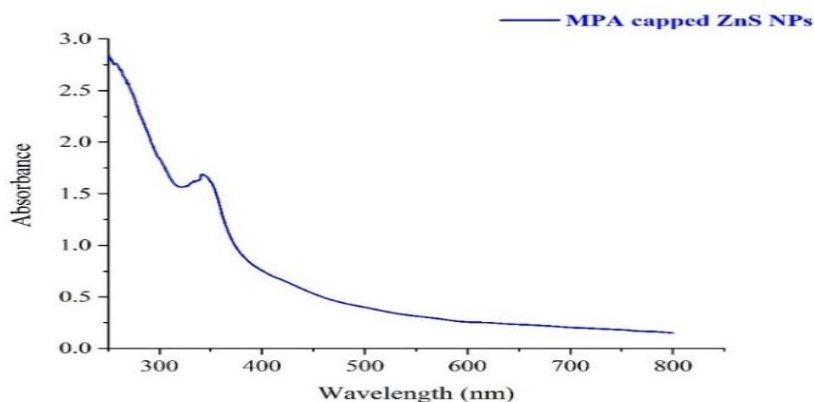


Figure 3: UV-Vis spectrum of MPA capped ZnS NPs (in basic medium)

Table 2: Calculated Band Gap Energy (E) and Sizes for the synthesized ZnS NPs.

NPs	Fluorescence Colour	Wavelength(nm)	Band Energy (eV)	Gap	Size (nm)
MPA-ZnS(basic medium)	Blue	323	3.84		2.04
MPA-ZnS:Cu	Green	243	5.10		2.70
MPA-ZnS:Mn	Green	243	5.10		2.70

The blue shift of the absorption peaks of the synthesized undoped and doped nanoparticles with the corresponding band gap energy (Table 2) are similar to those reported for ZnS NPs prepared through co-precipitation method using PVP, PVA and PEG-4000 as the capping agent at 312 nm, 321 nm, 327 nm and 266.18 nm respectively conforming to band gap values of 3.98 eV, 3.86 eV, 3.79 eV and 4.33 eV [7, 16]. In addition, the observed red shift in the band-gap energy of Cu-doped NPs from 3.84 -5.10 eV relative to undoped ZnS NPs is similar to those observed for Cu-doped ZnS NPs from 3.9 eV to 4.7 eV through co-precipitation method by annealing at 150 °C [17] although did not give the expected inverse effect on the particle size but rather influenced the optical property of the doped NPs.

Mercaptopropionic acid though a powerful reducing agent chelates the zinc ions during synthesis at lower pH. However, at higher pH (12), the dissociation of both side chains facilitates the replacement of the sulphide ion in the Zn-MPA-complex.

CONCLUSION

The study reports the synthesis of hydrophilic fluorescence doped and undoped Zinc sulphide NPs by simple low-cost one-step colloidal synthesis approach. The semiconductor obtained were investigated for ligand NPs surface chemistry for which the FT-IR result reveals band assigned to O-H_{str}, C=O_{str}, C-O_{str} and C-S that confirms effective interaction between the ligand and the NPs and also enhanced dispersibility. Furthermore, fluorescence study showed strong pale green and blue colour. The UV-Vis analysis revealed absorption peaks that corresponds to a blue shift in comparison with the bulk which therefore indicates the formation of NPs. The ZnS NPs observed in this study are envisioned to be candidate probe materials for bioimaging application.

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