Spectroscopic investigation of green synthesized ZnS nanoparticles encapsulated by sodium carboxy methyl cellulose

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Received: 24 June 2020 / Accepted: 23 October 2020 / Published online: 6 November 2020
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Abstract

In this article, the capping action of Sodium carboxymethyl cellulose (NaCMC) on ZnS nanoparticles synthesized by microwave-assisted method is reported. The X-ray diffraction and electron diffraction studies corroborated nanocrystalline nature of cubic ZnS. Discontinuous cluster growth of particles was implied by optical absorption studies. This was reflected in transmission electron microscope images. Fourier-transform infrared studies confirmed NaCMC capping on the surface of ZnS nanoparticles. Effective encapsulation of ZnS nanoparticles by NaCMC was further supported by Raman scattering, thermal studies and photoluminescence studies. Surface modification of ZnS nanoparticles with NaCMC appear to be suitable for specific biomedical applications due to the nontoxicity of ZnS and NaCMC.

Keywords ZnS nanoparticles · Biopolymer · Microwave irradiation · Optical properties · Thermal properties

1 Introduction

ZnS belongs to II–VI semiconductors with a wide band gap of 3.68 eV for sphalerite bulk phase. In addition to its low production cost and non-toxicity, ZnS is a thermally and chemically stable compound possessing a high dielectric constant of 8.7 [1]. Consequently, nanostructured ZnS finds itself in various fields such as super capacitors [2], solar energy applications [3], optical devices such as LED [4], biomedical applications [5][5] and luminescent display systems [7]. However, the nanosized ZnS particles are highly unstable and tend to agglomerate due to the surface effects of smallness in size. Therefore, confining the growth of nanoparticles (NPs) and providing surface passivation are of prime importance in the nanoparticle research. Biodegradable biopolymers offer an excellent opportunity in this direction.

Among naturally occurring biopolymers cellulose is most abundant one. Its derivatives have several advantages

such as recyclability, high viscosity, nontoxicity, biodegradability and cost effectiveness [8]. Sodium carboxy methyl cellulose (NaCMC) is a water-soluble cellulose derivative with carboxy methyl groups attached to some of hydroxyl groups of glucopyranose monomers of cellulose backbone. NaCMC has received ample scientific attention, due to its polyelectrolyte character [9]. In view of its high transparency, good film-forming property, large mechanical strength, non-toxicity and biodegradability, it is found suitable for applications such as medicine, flocculating agent, chelating agent, emulsifier, thickening agent, water-retaining agent, sizing agent, and film-forming material [10–12]. Recent reports on NaCMC reveal that it works as a stabilizer in the preparation of certain semiconducting nanosized materials like PbO nanoparticles [13], ZnO [14], CdS [15], ZnS [16] and some magnetic nanoparticles such as Fe₃O₄ [17, 18]. Increase in light emission intensity has been reported in ref [16]. for NaCMC stabilisation of ZnS films.

A detailed study of preparation of NaCMC-capped ZnS NPs and characterization is relatively less explored. In the present work, we report a novel synthesis approach for ZnS nanostructures using microwave-assisted aqueous precipitation technique. Microwave heating is a simple, fast and efficient method in which material heating takes place by dielectric heating [19]. In conventional heating, an external thermal source heats the reaction medium by a conductive heating. But microwave irradiation (MWI) causes efficient

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in-core volumetric heating by direct coupling of microwave (MW) energy with the molecules of solvents, reagents, catalysts, etc. that are present in the reaction mixture [19]. The quick and uniform heating of reaction mixture in MW heating induces fast homogeneous nucleation that leads to the formation of uniform sized small NPs [19], while prolonged hydrothermal conventional heating leads to form bigger particles with better crystallinity [20]. MW-assisted synthesis leads to the formation of more defects in the synthesized powders [21]. In unpassivated MW-synthesized nanoparticles, such defects on surfaces diminish the luminous intensity in them [22]. MW-assisted chemical reactions performed at the optimized reaction temperatures are found to be cleaner, produce less biproducts compared to conventionally heated processes [23].

Zinc acetate dihydrate (ZA) and thioacetamide (TA) were used as precursors for ZnS and NaCMC was used as the capping agent. The synthesis involves non-toxic precursors, solvent (water) and energy-saving principles of microwave heating such that most of the principles of green chemistry are followed. Very good photoluminescence behavior was exhibited by the properly capped sample.

2 Experimental

2.1 Chemicals

Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], thioacetamide (CH_3CSNH_2) and sodium carboxy methyl cellulose (NaCMC) were purchased from Alfa Aesar (Germany). All chemical reagents were of pure analytical grade and used without further purification. Double distilled (DD) water was used as solvent.

2.2 Synthesis of samples

The synthesis procedure followed in the present work is similar to that explained in ref [24]. and [4] with certain modifications. About 0.025 g of NaCMC was dissolved in DD water and aged for 24 h. To 0.15 M zinc acetate aqueous solution, NaCMC solution was added and mixed well by stirring. Thioacetamide (TA) solution at a concentration of 0.27 M in water was added to this. Total volume of the mixture was maintained to be 100 ml. The mixture was subjected to microwave irradiation in a domestic microwave oven (LG model: MS-2049UW of 20 L capacity operating at frequency 2.45 GHz) for predetermined 6 min. The reaction was evidenced by a change in the color from clear to milky white. After cooling, ZnS was separated from solution by centrifugation. Sample was dried and named as S1. Experiment was repeated for different amounts like 0.05, 0.075 and 0.1 wt % of NaCMC addition and samples were named as

S2, S3 and S4, respectively. At concentrations beyond 0.1 wt%, the solution was so viscous that collection of particles became difficult and the obtained sample was sticky. Pure sample of ZnS was also synthesized without the addition of NaCMC for comparison.

2.3 Characterization

X-ray diffraction (XRD) was carried out with Rigaku Mini-flex 600 X-ray diffractometer with monochromatic copper- K_α radiation of wavelength 1.5402 Å. TEM analyses were done by JOEL JEM 2100 high-resolution transmission electron microscope (HRTEM) and UV-Vis absorption studies were carried out using SHIMADZU – 1800PC spectrophotometer for the dilute dispersion of sample in DD water. The ZnS powders were dispersed in KBr pellets and FTIR spectra was obtained with NICOLET– 6700 spectrophotometer. Photoluminescence (PL) spectra were obtained with Hitachi F-7000 Fluorescence Spectrophotometer. Raman scattering experiments were performed using BRUKER RFS 27: Stand-alone FT-Raman Spectrometer. The thermal analysis was done using the thermal analysis instrument SDT Q600 V20.9 Build 20 in nitrogen atmosphere at a heating rate of 3°K/min for pure ZnS, ZnS-NaCMC composite S2 and neat NaCMC.

3 Results and discussion

3.1 X-ray diffraction

XRD patterns of ZnS-NaCMC nanocomposites and pure ZnS are shown in Fig. 1. The diffraction peaks are observed for 2θ values at 28°, 48° and 57°. The peaks are identified to originate from (111), (220) and (311) planes of the zinc blende structure of ZnS (JCPDS No. 01-072-4841). No peaks for other phases or elements are observed showing high purity of samples and the broad diffraction peaks is an indication of the particles in the nanometer dimension. The average nanocrystallite size (D) is determined for the prominent peak (111) using Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where λ is wavelength of incident X-rays; θ is angle of diffraction, β is full width at half maximum (FWHM) of Bragg peak. The NaCMC capped samples show slight increase in crystallite size compared to uncapped ZnS. Murugadoss et al. explained similar increase in crystallite size due to binding of surfactant on the ZnS nanoparticles [25]. But the nanocrystallites do not appear to change much in size with NaCMC concentrations. Interplanar separations (d_{hkl})

Fig. 1 XRD pattern for pure ZnS and ZnS-NaCMC composite samples

Table 1 Comparison of different parameters for pure and NaCMC-capped ZnS nanocrystals

Sample	NaCMC added (%wt.)	2θ (°)	Crystal-lite size D (nm)	Lattice constant <i>a</i> (Å)	Degree of crystallinity
ZnS-Pure	—	28.83	2.13	5.357	45.9
S1	0.025	28.86	2.27	5.352	58.1
S2	0.05	29.01	2.26	5.325	63.0
S3	0.075	28.93	2.27	5.339	56.8
S4	0.1	28.77	2.35	5.372	43.9

between the planes (hkl) are calculated using Bragg's law and lattice parameter '*a*' for cubic lattice is determined using:

$$a = d_{hkl} \times \sqrt{h^2 + k^2 + l^2}. \quad (2)$$

From the X-ray diffractogram, we have estimated degree of crystallinity using the ratio of area under crystalline peaks to the total area of crystalline peaks and amorphous regions [26]. The variation of nanocrystallite size, lattice parameter and degree of crystallinity for pure and NaCMC added ZnS samples are given in Table 1. Figure 2 depicts the variation of lattice constant and degree of crystallinity with NaCMC concentration. Lattice parameter is found to decrease with concentration of NaCMC, reaches minimum in the case of S2,

Fig. 2 Variation of lattice parameter and degree of crystallinity with NaCMC addition

and increases thereafter. The crystallinity increases with increase in concentration of NaCMC till 0.05% (S2) and decreases for further increase in concentration indicating good crystallinity for the sample S2. The improvement in crystallinity with NaCMC concentration is attributed to decrease in defects number due to the capping action of NaCMC, resulting in less imperfection in the crystallites. This continues up to 0.05 wt% concentration of NaCMC and thereafter crystallinity decreases due to aggregation of nanoparticles, seen in TEM micrograph.

3.2 UV–Vis spectroscopy

The plot of absorbance versus wavelength for all samples is shown in Fig. 3.

The excitonic absorption occurs at ~ 322 nm for pure ZnS while it occurs at ~ 332 nm for NaCMC-capped ZnS samples. These values are less than that for bulk counterpart which occurs at ~ 337 nm indicating that the particles are in nano-regime [28]. The appearance of sharp absorption maximum in Fig. 4 shows the monodisperse nature of nanoparticles [29]. With increasing concentration of NaCMC, the position of the absorption maximum remains almost same. This implies that nanoparticle growth is taking place not through Ostwald ripening, for, Ostwald ripening is recognized by the continuation of the excitonic absorption band towards larger wavelengths [30]. Instead, a well-defined absorption maximum occurs repeatedly, implying a discontinuous cluster

Fig. 3 Absorbance vs wavelength for S1, S2, S3 and S4. Inset is for pure ZnS sample

Fig. 4 **a** TEM image for ZnS-pure. **b** HRTEM image with inset showing electron diffraction pattern

growth of ZnS nanocrystals has taken place due to the anionic surfactant NaCMC. From XRD studies also, we observe that the size of coated NPs do not change much for the capped samples except for 0.1% NaCMC. The UV absorption curves show some absorption in the visible region and this is attributed to defect related states in the band gap [31].

From the studies above, it is apparent that sample S2 is better stabilized among the capped samples and this sample is selected for further analysis. To investigate about morphology, TEM and HRTEM images were taken for ZnS-pure, sample S2 and S4.

3.3 Electron microscopy

TEM and HRTEM images of ZnS-pure, samples S2 and S4 are shown.

TEM image shown in Fig. 4a for uncapped ZnS indicates the formation of solid spheres of size ~ 100 nm. The bigger size is due to the absence of capping agent. The lattice image (Fig. 4b) for ZnS-pure sample shows crystalline nature which is supported by SAED pattern. The SAED patterns in all cases indicate the polycrystalline behavior with phases (111), (220) and (311) of cubic ZnS.

In the case of sample S2, formation of spherical nanoclusters of near uniform size is shown by Fig. 5a. Each of these clusters can be seen to contain dispersed primary nanoparticles separated by a thin polymer layer.

In the HRTEM image of the coated nanoparticles (Fig. 5b), an ultrathin film of NaCMC polymer is clearly seen around ZnS nanoparticles and this film is bound intact to the nanoparticles. Good crystallinity of the sample is exhibited in the lattice image of the micrograph which was revealed by XRD studies also. Discontinuous lattice fringes indicate the polycrystallinity of the sample [32]. The size of NPs is estimated from the HRTEM image (Fig. 5b) the mean size is about 2.6 nm, which is similar to that of XRD results. It has been observed in nanoparticle physics that

Fig. 5 **a** Dispersed primary particles in the nanoclusters of sample S2 **b** Clearly observable lattice fringes and inset of (b) is electron diffraction pattern for S2

Fig. 6 Aggregated NPs of sample S4 and inset is SAED pattern for S4

semiconductor nanocrystals with crystallite size in the range of exciton Bohr radius show size dependent optical properties. The exciton Bohr radius for ZnS is about 2.5 nm.

Figure 6 shows the TEM image for sample S4. It reveals that, at high concentration of NaCMC, the ZnS NPs formed are aggregated in the matrix of NaCMC. However, the ZnS NPs formed in this case also exhibited cubic polycrystalline nature indicated by the diffraction pattern.

3.4 Fourier-transform infrared spectroscopy (FTIR)

FTIR is based on the principle that the chemical bonds can be excited at frequencies that are typical of the bonds and can provide valuable information about passivation of surface of nanoparticles by the polymer. Figure 7 shows the FTIR spectra for sample S2 and neat NaCMC. The broad

Fig. 7 FTIR spectra of NaCMC capped ZnS and pure NaCMC

absorption band at 3418 cm^{-1} for NaCMC corresponds to O–H stretching and the band at 2915 cm^{-1} corresponds to C–H stretching vibrations. The strong band at 1602 cm^{-1} and 1418 cm^{-1} are due to COO^- group [33]. The band at 1325 cm^{-1} is assigned to -OH bending vibrations [34, 35]. The characteristic -C-O stretching on polysaccharide skeleton is indicated by the absorption band at 1056 cm^{-1} . The band at 664 cm^{-1} is due to ZnS present in sample S2. The hydroxyl peaks of NaCMC shifted to lower wave number 3397 cm^{-1} for S2 indicating a strong interaction between hydroxyl groups of NaCMC and ZnS NPs [36]. The asymmetric and symmetric stretching vibrations at 2921 and 2849 cm^{-1} are due to -C–H vibrations and arise in S2 due to nanostructure formation [17, 37]. The band corresponding to COO^- shift to 1565 cm^{-1} . The presence of carboxyl and hydroxyl groups in the final ZnS-CMC compound is a strong confirmation that there is an interaction between zinc precursor and NaCMC molecule.

The growth of ZnS NPs and the capping action of polymer NaCMC may be understood from the chemical reactions involved in the synthesis. During synthesis, the Zn^{2+} ions formed in aqueous solution of zinc acetate make complexes with NaCMC added. This solution was microwave (MW) irradiated after the addition of thioacetamide (TA). MWI induces volumetric heating in the material due to inertial, elastic and frictional forces. The power absorbed by the material is represented by [38]:

$$P = 2\pi f \epsilon_0 \epsilon_r' \tan \delta E^2, \quad (3)$$

where f is frequency (GHz), ϵ_0 is permittivity of free space, ϵ_r' is relative dielectric constant, $\tan \delta$ is the loss factor and E is magnitude of internal field. As a result, MW irradiation affects the synthesis process in two ways. First, the polymer NaCMC decomposes during MWI to some extent and produce shorter chains which enable the Zn^{2+} ions to coordinate with $-\text{OH}$ ligands or make bond with COO^- groups [39]. Second, it accelerates the decomposition of TA to provide S^{2-} ions as:

As soon as S^{2-} ions become available, reaction between Zn^{2+} and S^{2-} ions takes place to form ZnS nuclei. ZnS nuclei formed grow into nanoparticles under the combining force between Zn^{2+} ions and S^{2-} ions within the cavities bound by the polymer chains [40]. NaCMC being anionic long chain polymer, provides electrostatic as well as steric stabilization. Hence, an increase in crystallite size is observed for NaCMC-capped samples compared to uncapped ZnS. At lower concentration of NaCMC, the availability of fewer $-\text{CH}_2\text{COO}^-$ ligands attached to NaCMC lead to incomplete coverage of ZnS NPs. For concentrations of NaCMC like, 0.05% the NaCMC serves as a shell and final particles formed are nearly spherical, possess uniform size and can disperse well in water [11]. For higher concentrations like 0.1%, the space between polymer chains becomes narrower as a result of increased viscosity [32]. The increased number of polymer chains now provides more carboxyl and hydroxyl linkages to Zn^{2+} ions leading to the formation of large number of ZnS nuclei in a small space. Hence, the decrease in crystallinity observed with samples S3 and S4 compared to S2 may be attributed to the aggregation.

3.5 Photoluminescence (PL) spectroscopy

The influence of NaCMC capping on the photoluminescence (PL) of ZnS NPs is investigated and PL graphs are shown in Fig. 8. The samples were excited at 250 nm. The

Fig. 8 Photoluminescence spectra for S2 and inset is for pure ZnS

luminescence observed with ZnS- Pure and sample S2 indicate visible emission. Hence emission phenomenon involves localized states in the band gap. The PL spectra obtained are broad and asymmetric, consisting of more than one component. Gaussian curve fitting was applied to deconvolute the PL peaks. The best Gaussian fit gave five peaks for pure ZnS. Weak emission at 350 nm is attributed to S interstitials [I_S] and peak at 363 nm is attributed to Zn interstitials [I_Zn]. The strong peak centered at 391 nm is assigned to the recombination of electrons at the excess Zn present [41]. Peak at 442 nm is attributed to transition from surface sulfur vacancy [SV_S]. Emission peak near 469 nm is due to internal S vacancy [V_S] to internal Zn vacancy [V_Zn] [42].

In the case of NaCMC-capped sample, the peak at 355 nm is attributed to interstitial S [I_S] ions. As the radius of S ions is larger than that of Zn ions, interstitial S causes greater strain and possess less binding energy. Corresponding energy levels lie close to valence band and energy levels for Zn interstitials lie close to conduction band. Zn-related emission occurs at 399 nm. Peak near 470 nm is assigned due to internal S and Zn vacancies. Surface sulfur vacancy related emissions are not observed for NaCMC capped sample.

Energy-dispersive X-ray analysis showed that the amount of sulfur is less compared to zinc in the capped as well as uncapped samples which may give rise to sulfur vacancies at the surface causing Zn dangling bonds and form shallow donor levels. But in the emission spectra of capped sample, no band corresponding to surface sulfur vacancy is found indicating the strong coupling of dangling bonds of ZnS with NaCMC. As supported by FTIR, there is bonding between NaCMC and excess Zn^{2+} ions present on surface of ZnS nanoparticles.

The important difference between PL spectra of pure ZnS and S2 is in the number of PL peaks and their intensity. In pure-ZnS, due to surface sulfur and surface zinc related

5 emission peaks were observed, but on capping, these emissions were absent. The capped ZnS is having more PL intensity owing to controlled homogeneous growth of the nanoparticles in solution medium. The higher PL intensity in NaCMC-capped sample is attributed to better passivation of surface-related defects, leading to an increase in electron–hole recombination [43, 44]. The low PL intensity observed with ZnS-Pure is due to the presence of surface defects which cause nonradiative decay.

Schematic of the photoemission in S2 is represented by Fig. 9.

3.6 Raman scattering

Raman spectroscopy is a fast and useful technique to analyze surface properties of nanosized particles. Figure 10 corresponds to the room temperature Raman spectra of sample S2 and neat NaCMC obtained using excitation source of wavelength 1024 nm. The excitation energy is in off-resonance regime for ZnS. Bands observed for capped ZnS nanoparticles near 260 cm^{-1} and 343 cm^{-1} are assigned to transverse optical (TO) and longitudinal optical (LO) modes, respectively, for cubic phase of ZnS. For bulk ZnS, these bands were reported to occur at 276 cm^{-1} for TO and 351 cm^{-1} for LO modes [45]. The larger Raman shift from bulk in the present study may be due to the effect of phonon confinement resulting from the small size of particles ($\approx 2.3\text{ nm}$). Some of the skeletal and carboxylate ion related vibrations due to NaCMC also occur in S2. The assignment of Raman vibrations for neat NaCMC and S2 are derived from the literature [46–48] and given in Table 2. The appearance of Raman modes of vibration for NaCMC along with that for ZnS in sample S2 indicates the interaction of NaCMC with ZnS NPs.

There were no Raman bands around 286 cm^{-1} corresponding to wurtzite phase [45]. This is in accordance

Fig. 9 Schematic of PL emission for S2

Fig. 10 Raman spectra for NaCMC and sample S2

with XRD results which show peaks corresponding to cubic ZnS only.

3.7 Thermal properties

Thermo gravimetric analysis (TGA) plays an important role in determining thermal stability of the materials. To understand the thermal behavior of the ZnS-NaCMC composite, TGA were performed for ZnS-pure, sample S2 and neat NaCMC. TGA curves are shown in Fig. 11. In all curves, the initial loss in weight is due to the loss of adsorbed gases from the surface. For sample S2 and neat NaCMC, the second loss in weight occurs due to the loss of CO_2 from the Cellulose. In this temperature range, the decarboxylation of COO^- group in CMC takes place which demonstrates the decomposition of CMC [49]. Neat NaCMC experienced a 50% weight loss at a temperature of $\sim 300^\circ\text{C}$, whereas for sample S2, it was only 15% weight loss at temperature $\sim 450^\circ\text{C}$. The TGA curve for neat NaCMC is steep between 250°C and 300°C while sample S2 shows broader decomposition temperatures in the range 250°C – 450°C , indicating a better thermal stability of S2 compared to NaCMC [50]. The drastic decrease in mass for pure ZnS and sample S2 beyond 600°C indicates the decomposition of ZnS into its constituents.

Table 2 Assignment of Raman bands for NaCMC and S2

Raman peak position in NaCMC (cm ⁻¹)	Raman peak position in Sample S2 (cm ⁻¹)	Approximate assignment
—	260	ZnS TO mode
—	343	ZnS LO mode
893	934	Cellulose backbone
1109	1110	-COC glycosidic stretching
1245	1256	CH ₂ twisting mode
1327	1346	CH ₂ wagging
1418	1420	Symmetric stretching of COO ⁻
1601	1610	Asymmetric stretching of COO ⁻

Fig. 11 TGA curves of ZnS-pure, sample S2 and inset is TGA curve for NaCMC

Some of the properties of the sample S2 are presented in the following Table 3 along with the results obtained in other published works.

In all, we have seen that, the ZnS nanoparticles when properly capped with NaCMC, becomes a good light emitter. By studying magnetic nature of these NPs, this work can be extended for targeted drug delivery.

4 Conclusions

In summary, microwave assisted synthesis of NaCMC capped ZnS NPs was carried out by chemical precipitation method. From the studies on structural and optical properties of samples, following conclusions were drawn:

- Powder XRD and TEM studies indicated that the synthesized samples of ZnS possessed sphalerite structure with average nanocrystallite size less than 3 nm. NaCMC-capped ZnS showed increase in nanocrystallite size compared to uncapped one. But it did not increase with concentration of NaCMC which was supported by UV-absorption studies. Blue shift of UV-Vis absorption peaks indicated quantum size effect.
- The surface shallow defect related emissions of ZnS were quenched with NaCMC capping. A very good enhancement in photoluminescence intensity was observed with NaCMC-capped sample compared to uncapped ZnS.
- FTIR and Raman studies suggested that capping action of NaCMC onto ZnS takes place through the linkages of -OH and COO⁻ ligands.
- The thermal studies also confirmed the interaction of NaCMC with ZnS.

Table 3 Comparison of some physical parameters of ZnS structures grown by different techniques

Ref	Method	Capping agent	Sulfur source	Crystallite size from XRD (nm)	Strain in crystal	Shape of nanostructure
Present work S2-sample	Microwave irradiation	Sodium carboxy methyl cellulose	Thio acetamide	2.26	0.0612	Nanospheres
[51]	Chemical precipitation	–	Thio urea	4	–	Star like
			Sodium sulfide	4	–	Star like
[52]	Chemical precipitation and Chemical bath deposition	Ethylene diamine	Thioacetamide	4.5	–	No analysis done
				8	–	Thin film on Si substrate
				<4.5	–	Isosceles triangular surface seen in AFM
						Thin film on glass substrate
						Square like surface seen in AFM
[53]	Microwave Assisted synthesis	Tetrabutyl ammonium hydroxide	Thio urea	20.7	0.0010	Irregular spherical structures
[23]	Microwave Assisted synthesis	Polyvinyl pyrrolidone (PVP)	Na ₂ S	–	–	Particles with large aggregation effects
[54]	Chemical precipitation	L-cysteine	Na ₂ S	2.10	–	Monodispersed particles with less agglomeration after capping

Acknowledgements The authors thank Bhandarkars' Arts and Science college, Kundapura for sample preparation facilities, DST PURSE Laboratory, Mangalore University – Mangalore for thermal analysis, DST- SAIF centre, IIT Madras at Chennai for Raman scattering experiments, DST- SAIF centre at Karnatak University-Dharwad for FTIR and photoluminescence measurements and Manipal Academy of Higher Education—Manipal for other characterizations. Author Lalitha Devi B thanks the University Grants Commission, Government of India, for teacher fellowship.

Funding Open access funding provided by Manipal Academy of Higher Education, Manipal.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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