

Understanding the role of surfactants on the preparation of ZnS nanocrystals

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Abstract

We have synthesized surface modified ZnS nanoparticles of size 2–3 nm using non-ionic surfactant-stabilized reverse emulsions. The non-ionic surfactants in the Span series, i.e. sorbitan monolaurate (Span 20) and sorbitan monooleate (Span 80) of hydrophilic–lipophilic balance (HLB) values of 8.6 and 4.3, respectively, have been used for the stabilization of emulsions. The role of these surfactants in controlling the size and properties of the ZnS nanoparticles has been discussed. The triethylamine (TEA) has been proved to be the effective surface modifying (capping) agent for the preparation of free-standing ZnS nanoparticles. The Span 20 with the higher HLB value of 8.6 has been found to be highly suitable in synthesizing TEA-capped ZnS nanoparticles of smaller size and higher photophysical characteristics compared to that of the Span 80 of lower HLB value of 4.3. A mechanism for the formation of TEA-capped ZnS nanoparticles from the surfactant-stabilized reverse emulsions has been proposed.

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1. Introduction

Semiconductor nanocrystals have attracted a lot of interest in recent years owing to their special electronic and optical properties due to quantum confinement effect [1–5]. Various wet chemical methods have been developed for the synthesis of these nanoparticles [6–10]. Synthesis of these nanoparticles with narrow size distribution is an essential requirement for practical purposes. Further, the optical properties are strongly dependent on the technique adopted for the chemical synthesis of these nanoparticles. Among other methods, reverse emulsion method is a well-accepted method for the synthesis of these nanoparticles due to several advantages. In our previous study, we have already seen the effect of non-ionic surfactants in tailoring the size of the alumina microspheres. In the present study, we will examine the role of these surfactants in synthesizing ZnS nanoparticles and their effects on photophysical properties which is not yet well studied. Keeping the above points in view, in the present investigation we report a reverse emulsion

technique for the synthesis of triethylamine (TEA)-capped ZnS nanoparticles. In the present investigation, the two immiscible liquids, i.e. for the w/o in oil type emulsions (reverse emulsion), i.e. dispersion of the water phase (aqueous Zn^{2+} in this study) in the oil phase (cyclohexane) are used. It is known that thermodynamically, the increase in surface area (ΔA) of the dispersed phase associated with a free energy (ΔG) can be represented as [12]

$$\Delta G = \gamma \Delta A, \quad (1)$$

where γ is the interfacial tension. The equation indicates that a low interfacial tension favours droplet disruption. In fact, the high interfacial tension between the dispersed water phase and continuous oil phase is reduced by the addition of a system compatible amphiphilic surface active agent or surfactant (emulsifier in the present case), i.e. the molecule with a polar head and a non-polar tail [12]. The surfactant molecules orient themselves according to the polarities of the involved chemical constituents. Thus, due to the high polarity of water, the polar heads of the surfactant molecules at the water–oil interface are oriented towards the water droplets and get adsorbed on their surfaces and prevent the coalescence of the droplets by steric hindrance occurring between two droplets (steric stabilization).

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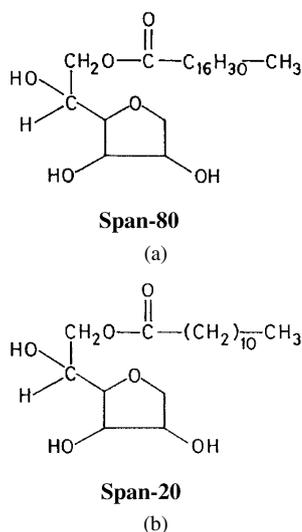


Fig. 1. Molecular structures of (a) Span 80 and (b) Span 20.

Therefore, the emulsifier added to the system: (i) lowers the interfacial tension between two immiscible liquids followed by droplet disruption and (ii) prevents re-coalescence of droplets by adsorbing on their surfaces, thus producing a stable emulsion. In the present investigation, Span 80 and Span 20 stabilized reverse emulsions comprising aqueous Zn^{2+} solutions and cyclohexane as the water and oil phases, respectively, were used for the synthesis of ZnS nanoparticles. The surfactants in the Span series, i.e. Span 80, and Span 20 in the present case, are basically the fatty acid esters of anhydro sorbitols which are good oil soluble emulsifying agents [12]. A high (hydrophilic–lyophobic balance) HLB value of the surfactant indicates strongly hydrophilic character while a low value is an indication of a strong hydrophobic nature. Considering these points, non-ionic surfactants, i.e. Span 80 and Span 20 with HLB values of 4.3 and 8.6, respectively, were selected for the present study. Figs. 1a and 1b depict the molecular structures of the amphiphilic Span 80 and Span 20, respectively, [11] where the hydrophilic sorbitan group acts as a ‘polar head’ and the hydrophobic fatty acid group acts as the ‘non-polar tail.’ The effect of the type of the surfactants on the photophysical properties of the nanocrystals is discussed. A mechanism for the separation free-standing ZnS nanocrystals from the stabilized emulsion is suggested.

2. Experimental

2.1. Synthesis of TEA-capped ZnS nanoparticles

In the present investigation, water-in-oil (w/o) type emulsions were used for the synthesis of ZnS nanoparticles. For such synthesis, zinc acetate, dihydrate (A.R., Glaxo, India) and thioacetamide [$\text{CH}_3(\text{CS})\text{NH}_2$] (G.R., Loba Chemie, India) were used as the starting materials. An aqueous solution of zinc acetate with Zn^{2+} concentration of 0.05 M and thioacetamide of concentration of 2.5 M was prepared by dissolving the respective salts in deionized water. The two solutions were mixed under stirring in the 1:1 volume ratio so as to obtain a mixed ho-

mogeneous solution; this mixed solution was used as the water phase (w) of w/o type emulsions. An organic solvent, i.e. cyclohexane (G.R., Merck, India) of dielectric constant 2.042 [8,11] at 25 °C acted as the oil phase (o). A support solvent was prepared by mixing 5 vol% of the surfactant, sorbitan monooleate (Span 80) with HLB value of 4.3 (Fluka Chemie AG, Switzerland) in the cyclohexane. For the preparation of the w/o type emulsions, the water phase was dispersed as droplets in the support solvent under a constant mechanical agitation of 500 rpm and kept under such condition for 10 min for equilibration. The volume ratio of the water phase: support solvent was kept constant at 1:4 in all the experiments.

The stabilized emulsion was then placed in an oil bath pre-set at 80 ± 1 °C. The emulsion was aged at 80 ± 1 °C for 10 min under stirring (500 rpm) and then removed from the bath. The entire emulsion was added to a known volume of acetone (G.R., Merck, India) (volume ratio of emulsion:acetone = 1:3) when the pH of the system was found to be 6. At this stage, sedimentation of the nanoparticles did not occur. To prepare free-standing capped-ZnS nanoparticles, the pH of the above system was then increased to 8 by the addition of triethylamine (TEA) (G.R., Merck, India). Immediate flocculation of particles occurred which were collected by centrifugation at 6000 rpm. To remove last traces of adhered impurities, the particles were washed thrice with acetone, each time collecting the particles centrifugally as described above, followed by the dispersion in the washing solvents. The washed particles were dried at 60 °C. Following the same procedure another experiment was conducted using the surfactant Span 20.

2.2. Characterization of the sulphide nanoparticles

The ZnS nanoparticles were characterized by XRD (Model: Philips, 1730, USA) with Ni-filtered $\text{Cu-K}\alpha$ radiation, FTIR study (Model: Nicolet 5PC, USA), and TEM (Model: JEOL JEJ-200X, Japan). Fluorescence spectra of ZnS nanoparticles dispersed in ethanol were recorded with a spectrofluorimeter (Model: LS 55, Perkin Elmer, USA) in the wavelength range of 200–650 nm. Optical absorbance of the ZnS particles were recorded with an UV–vis spectrophotometer (Model: Cary 50, Varian) in the range 200–500 nm.

3. Results and discussion

3.1. Formation of ZnS nanoparticles

The metal ions in the emulsified aqueous microdroplets were precipitated as sulphides by H_2S , in situ generated at 80 ± 1 °C via thermal decomposition of the thioacetamide [8]. The particle size in the microreactor was tailored by controlling the reaction temperature, ageing time and the concentration of Zn^{2+} ions in the aqueous solutions. Based on the experimental results, the ageing time of 10 min at the reaction temperature of 80 ± 1 °C and the concentration of Zn^{2+} ions of 0.05 M were found to be the optimum. The particle size was further tailored by using surfactants of two different HLB values, keeping other

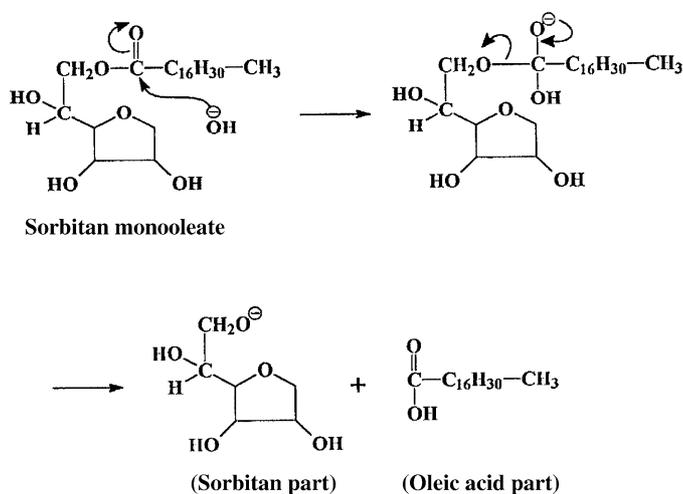


Fig. 2. Proposed mechanism for the separation of TEA-capped ZnS nanoparticles.

parameters unaltered. Considering the HLB values and structures of the surfactants (Fig. 1) used in the present study, it is to be noted that the HLB value, i.e. the hydrophilicity, decreases with the increase in the hydrophobic chain length. Further, an inverse relationship between the average particle size and the HLB values of the surfactants was reported earlier during the synthesis of alumina microspheres by the sol-emulsion-gel method [11]. This was explained to be due to the fact that an increase in the HLB value caused a gradual decrease in the water-oil interfacial tension, thus facilitating droplet disruption and finally giving rise to particles of progressive decreasing size.

In our study, free-standing ZnS nanoparticles were obtained in both the Span 80- and Span 20-stabilized reverse emulsions, by increasing pH to 8 by the addition of TEA. The proposed mechanism for the separation of ZnS nanoparticles in presence of TEA is presented in Fig. 2. At pH 6, before the addition of TEA, ZnS nanoparticles formed complex with oxygen atoms of the polar heads of the surfactant molecules and caused an increase in apparent solubility in the acetone medium [13]. In presence of TEA, at pH 8, the above-mentioned ZnS complex became destabilized due to the basic hydrolysis of the surfactant molecules (the fatty acid esters) attached to the nanoparticles and formed new complex (capped) with the nitrogen atom of TEA molecules. The solubility of TEA-capped ZnS nanoparticles decreased in the acetone medium, leading to the flocculation as free-standing particles. The basic hydrolysis of the surfactant molecules is considered to be consisted of the following essential steps:

- (i) The TEA molecule in presence of H_2O form triethylammonium hydroxide

$$(\text{C}_2\text{H}_5)_3\text{N} + \text{H}_2\text{O} \rightarrow (\text{C}_2\text{H}_5)_3\text{N}^+\text{HOH}^-.$$
- (ii) The triethylammonium hydroxide increases the pH of the system by liberating hydroxide (OH^-) ions.
- (iii) The (OH^-) ion attacks the carbon (C) atom of the ester carbonyl ($>\text{C}=\text{O}$) group in the surfactant molecule (sor-

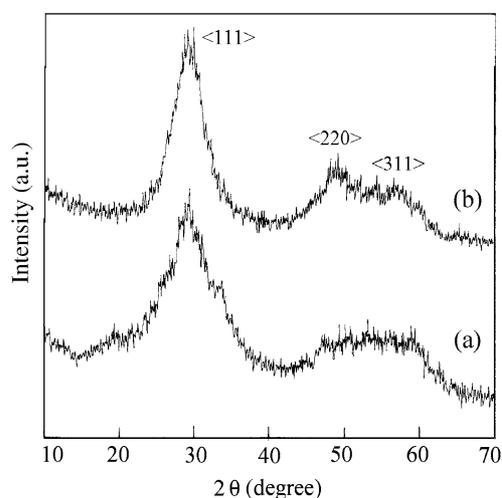


Fig. 3. XRD patterns of TEA-capped ZnS nanoparticles using (a) Span 20 and (b) Span 80.

bitan monooleate as a typical example), causing hydrolysis into the sorbitan and oleic acid parts (Fig. 2).

- (iv) Hydrolysis of the sorbitan monooleate destabilizes the emulsion system followed by the flocculation of the generated particles.

Formation of TEA-capped ZnS nanoparticles is confirmed by XRD and FTIR studies described in the subsequent sections. The effect of the nature of the surfactants and their HLB values on the characteristics of the nanoparticles has been examined by the UV-vis absorption and photoluminescence studies.

3.2. XRD and FTIR studies

Fig. 3 a and b represent the powder XRD patterns of the TEA-capped ZnS nanoparticles prepared by our method with surfactants Span 80 and Span 20, respectively. It is to be noted that in both the figures the peaks observed in the XRD patterns match well with those of the β -ZnS (cubic) reported in the JCPDS Powder Diffraction File No. 5-0566. Intensities of the three most important peaks of ZnS, namely $\langle 111 \rangle$, $\langle 220 \rangle$ and $\langle 311 \rangle$ reflections corresponding to 28.5° , 47.6° and 56.4° respectively, do not deviate from the Powder Diffraction File intensities [14]. Broadening of the XRD peaks shows the formation of nanocrystals of ZnS. XRD patterns also indicate that the peaks in Fig. 3b are broader than those in Fig. 3a. Crystallite size of ZnS nanoparticles were calculated following the Scherrer's equation [8,14] using $\langle 111 \rangle$ reflection of the XRD patterns and are estimated to be 2.4 and 1.8 nm for Fig. 3, a and b respectively. XRD results, therefore, indicate the formation of smaller size ZnS particles from the Span 20-stabilized reverse emulsion compared to that obtained from the Span 80.

The presence of TEA in the synthesized ZnS nanoparticles was examined by recording their FTIR spectra in the range $4000\text{--}400\text{ cm}^{-1}$. Fig. 4 depicts the spectra of TEA-capped ZnS nanoparticles derived from Span 80-stabilized emulsion as a typical example. From Fig. 4, it is to be noted that the absorption peaks at 3431 and 1631 cm^{-1} in the figure are assigned

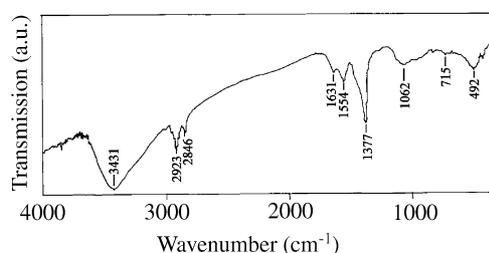


Fig. 4. FTIR spectrum of TEA-capped ZnS nanoparticles.

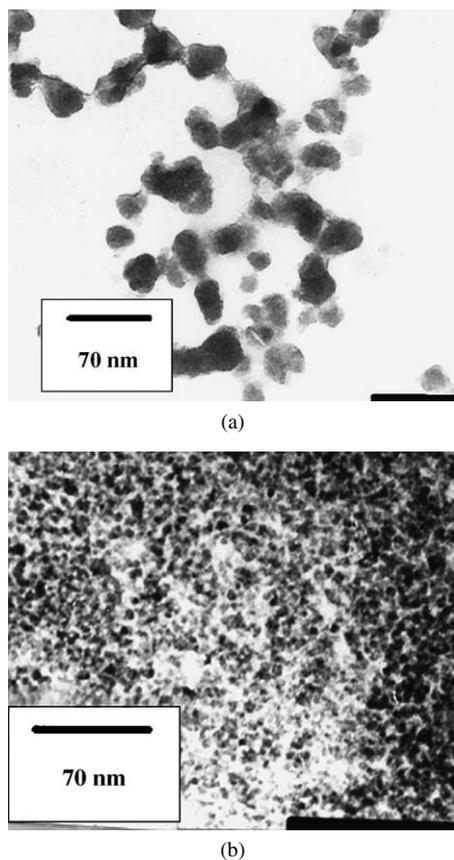


Fig. 5. TEM micrographs of ZnS nanoparticles using (a) Span 80 and (b) Span 20.

to water molecules and hydrogen bonded hydroxyl groups respectively [14,15]. Other peaks observed mainly at 2923, 2846, 1554, 1445, 1377 and 1062 cm^{-1} are due to C–H bonding [14,15]. This is due to the formation of co-ordinate bond between the nitrogen atom of the TEA and Zn^{2+} ions [14,15]. Therefore, from the FTIR results in the present study, capping of ZnS nanoparticles with TEA molecules is assured in our samples. The effect of particle size on the UV–vis absorption and PL studies has been discussed below.

3.3. TEM study

The TEM micrographs of the Span 80- and Span 20-derived TEA-capped nanoparticles are depicted in Figs. 5a and 5b respectively. In both the micrographs, the particles are mono-dispersed in nature and the size was estimated to be in the range 2–3 nm which corroborated with the XRD results.

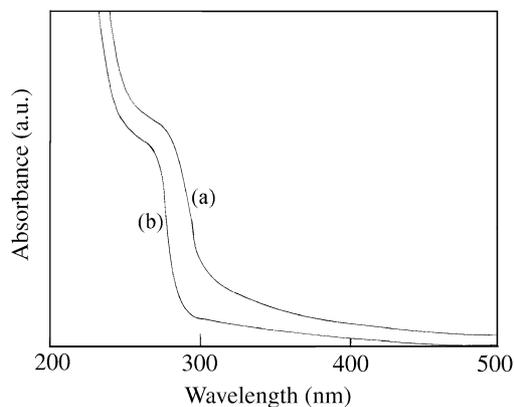


Fig. 6. UV–vis absorption spectra of ZnS nanoparticles using (a) Span 80 and (b) Span 20.

3.4. UV–vis absorption and PL studies

UV–vis absorption spectra of TEA-capped ZnS nanoparticles obtained from Span 80- and Span 20-stabilized reverse emulsions have been presented in Fig. 6 a and b, respectively. Fig. 6a exhibits the absorption edge at 303 nm with a shoulder peak at 285 nm, while in Fig. 6b the absorption edge at 290 nm with a shoulder peak at 272 nm is noticed. Absorption edges in Fig. 6, a and b exhibit blue shifts in comparison to bulk ZnS (345 nm). This shift of the absorption edges to shorter wavelengths is explained due to the quantum confinement of ZnS nanoparticles [6,14]. The absorption edges of the nanocrystallites are also sharp, indicating that the synthesized particles have relatively narrow size distributions. Here, we calculate the cluster size of ZnS using the following equation [16,17]

$$\Delta E = \pi^2 \hbar^2 / 2\mu r^2 - 1.78e^2 / \epsilon r, \quad (2)$$

where ΔE is blue shift band gap and μ is the reduced mass of electron and hole. 0.2 is taken as the electron rest mass m_0 , r is the cluster size and ϵ is the dielectric constant. The first term indicates the confinement effect and the second term is the Coulomb term. In a strong confinement, as in the present case, the second term is small and can be neglected. Based on Eq. (2), the cluster sizes of Span 80- and Span 20-derived ZnS have been found to be 2.1 and 2.6 nm respectively, which is fairly consistent with those obtained from the XRD study. Therefore, from the optical absorption study we infer that the surfactant Span 20 with the higher HLB value of 8.6 successfully produced smaller ZnS nanoparticles compared to that obtained from the Span 80 of lower HLB value.

The PL spectra of the Span 80- and Span 20-derived TEA-capped ZnS nanoparticles are presented in Fig. 7 a and b, respectively. The band edge emissions peaking at 379 and 373 nm are observed for the samples corresponding to Fig. 7 a and b, respectively. In both the spectra, PL peaks are markedly blue shifted (about 65 nm) relative to that of bulk ZnS (440 nm) and thus exhibiting quantum size effects [14,17]. The interesting point is that under identical conditions of synthesis, the Span 20-derived nanoparticles exhibit highly intense (about eight times) PL emission than that of the Span 80-derived nanoparticles. Further, the narrow emission band width of the

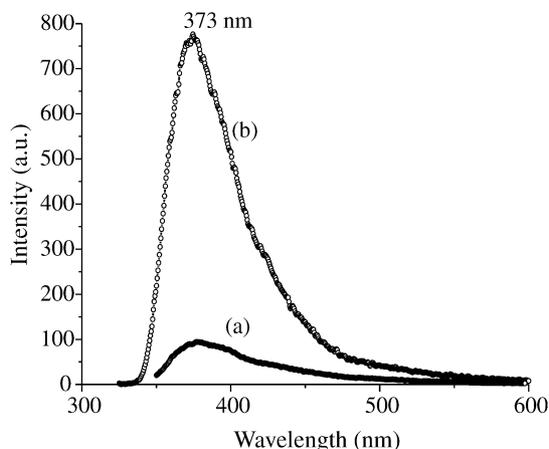


Fig. 7. Photoluminescence spectra of ZnS nanoparticles using (a) Span 80 and (b) Span 20.

same sample indicates a relatively narrow size distribution of the particles. The red shifting of the PL peak to 379 nm for the Span 80-derived ZnS nanoparticles compared to that of at 373 nm of the Span 20-derived particles, explains the formation of smaller particles in the Span 20-derived particles. The PL emission in both the samples was assigned to the interstitial sulphur lattice defects [14,18]. Therefore, PL studies further prove the formation of smaller sized ZnS nanoparticles from the Span 20-stabilized reverse emulsions compared to that from the Span 80. This happens because Span 80 with low HLB value of 4.3, produced large size microdroplets and caused more ZnS particle formation via precipitation which subsequently formed larger particles by Ostwald ripening during ageing at the reaction temperature compared to that of Span 20 of higher HLB value of 8.6.

4. Summary

We have reported a soft chemical method for in situ synthesis of monodispersed, TEA-capped ZnS nanoparticles using two different surfactant-stabilized w/o type reverse emulsions. Two types of non-ionic surfactants in the Span series, i.e. Span 80 and Span 20 with the HLB values of 4.3 and 8.6, respectively, have been used for the stabilization of emulsions in the present study. A mechanism for the generation of TEA-capped ZnS nanoparticles from stabilized emulsions has been suggested. The role of surfactants on the characteristics of ZnS nanoparticles has been discussed. XRD reveals that the synthesized nanoparticles exhibit zinc blende (cubic) structure. Crys-

tallite size measured from XRD peaks proves the formation of smaller (1.8 nm) ZnS nanoparticles from the Span 20-stabilized emulsions compared to that (2.4 nm) of the Span 80. Formation of TEA-capped nanoparticles is confirmed by the FTIR studies. TEM micrographs exhibit well-defined, monodispersed ZnS nanoparticles of size 2–3 nm which corroborates with the XRD results. UV–vis absorption and PL studies further prove that the nanoparticles with comparatively smaller size and narrow size distribution obtained from Span 20-stabilized reverse emulsion exhibited strong quantum size effect and highly intense PL characteristics compared to that of the Span 80-derived one.

Acknowledgments

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