ABSTRACT

Raspberry-like ZnS nanoparticles were synthesized by hydrothermal method. ZnS particle size varies by controlling the amount of comb polycarboxylic acid surfactant and polystyrene (PS) template. The products were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy, and Fourier transformed infrared spectroscopy. Optical properties were investigated via UV-vis and photoluminescence spectrophotometry. All samples consisted of ZnS cubic phase ( sphalerite ). The XRD patterns showed that surfactant has a vital effect on crystallite size reduction. In contrast, PS template enhanced the growth rate of ZnS nanoparticles. Studies on morphology and particle size showed that increasing the amount of surfactant content causes the ZnS particle size to decrease to nanometric range. Although particle size increased by deposition of ZnS nanoparticles on the surface of PS template, the uniformity of the particles increased considerably. A narrow range of particle size distribution (110-150 nm) was shown in the sample synthesized in the presence of both surfactant (2.2 g/L) and PS template (1 cc of 2.7% w/v). The blue shift of absorption edge in UV-vis spectra with an increase in surfactant content demonstrated the quantum confinement effect of ZnS nanoparticles. The obtained ZnS nanoparticles displayed blue emission peaks at 400 and 425 nm. Furthermore, a schematic model is proposed illustrating ZnS formation on the surface of PS template in the presence of the anionic surfactant.

INTRODUCTION

The most important colloidal quantum dots (QDs) like ZnS, CdS, ZnSe, CdTe and PbSe emit light from the UV to the infrared region. The development techniques of producing colloidal quantum dots in solution have led to a dynamic growth in research on these materials. Due to this, the new concepts of artificial solid could be employed in a much wider range of applications [1,2]. Many of such nanostructures also exhibit fascinating optical properties that could significantly impact the photonic technology in the near future [3]. Moreover, semiconductor nanoparticles play a major role in several new technologies in the fields of displays, lighting, sensors and lasers. Transition metal ions and/or rare-earth metal ions doped ZnS nanoparticle are amongst the most popular topics of semi-
ZnS nanoparticles are synthesized by different methods, such as microemulsion [5], colloidal precipitation [6], thermal evaporation [7], and etc. Recently, more attention has been paid to the synthesis of nanocrystalline ZnS powder via hydrothermal process. The main reasons for this attention are related to the potential capability of hydrothermal process for achieving special morphologies (spindle-like, microtubular, spherical, nanorods, nanosheets, and etc.) and different phases (sphalerite and wurtzite). The variation of pressure in the hydrothermal process generally leads to submicron but nanocrystalline ZnS particles without requiring further calcination step [8-11]. However, the synthesis of quantum dot ZnS nanospheres is possible via hydrothermal technique using a proper surfactant agent [12].

Recently, preparation of inorganic-organic (I/O) hybrid materials having controlled size and morphology has attracted much attention in the field of nanoscience and nanotechnology. The I/O materials will play an important role in electronic and optoelectronic devices in the future [13,14]. ZnS hybrid particles are mainly used as photonic crystals and optical materials. Self-assemble formation of ZnS shell on the surface of a polymer template leads to the improvement of photonic and optical properties of ZnS particles [15-17]. Most research activities on the synthesis of ZnS hybrid particles have been focused on PS template. Pich et al. [18] showed that uniform ZnS shell deposits on the surface of PS particles in the presence of β-diketone surface groups (PS/AAEM). Liddell et al. [19] employed the chemical bath deposition method to synthesize PS core-ZnS porous shell particles. Recently, ZnS or CdS hollow spheres were fabricated using PS nanospheres as a template [20,21]. Moreover, the steric effect of polymer chains grafted on the surface of ZnS particles prevents these particles from agglomeration. In this regard, PVP forms the excellent I/O ZnS-PS hybrid particles. The main role of PVP is to cover the ZnS nanoparticles surface via physico-chemical bonding, which reduces particle-particle interaction, and thus avoids agglomeration of the nanoparticles. Beside deagglomeration, the growth rate of ZnS particles covered by PVP would be greatly reduced, leading to normal and regular growth of ZnS particles [22]. During the deposition of ZnS shell on the surface of PS, the PVP prevents from agglomeration and controls the shell thickness [19]. As far as we know, there is a little work on the synthesis of ZnS nanoparticles by hydrothermal method in presence of surfactant. Moreover, hydrothermal synthesis of ZnS nanoparticle in the presence of polymer template has not been reported yet. In this paper, the controlling parameters such as nano-polystyrene template and polymeric surfactant on formation of ZnS nanoparticles in hydrothermal synthesis process have been investigated.

**EXPERIMENTAL**

**Materials**

Zinc acetate hydrate (99.99%, Merck, Germany), thio-acetamide (TAA, Merck, Germany) (99%), polyvinyl pyrrolidone (PVP, Aldrich, Germany) and potassium persulphate (KPS, Merck, Germany) as the free radical initiator were analytical grades. Styrene monomer and sodium dodecyl sulphate (SDS) were used as the ionic surfactant. The anionic surfactant used in this paper was an acrylic polyester/polyether copolymer with carboxylic groups in copolymer backbone. PS Template and anionic surfactant were prepared in ICST (Institute for Color Science and Technology Tehran, Iran). All chemicals were used as received without any further purification.

**Preparation of Polystyrene Template**

Polystyrene (PS) latex preparation was carried out using emulsion polymerization technique. Initially, known amounts of distilled water (500 mL) and surfactant (1 g) were transferred into a 2-L glass beaker and degassed by nitrogen purging for 15 min. The styrene monomer was charged into the reactor while the temperature was adjusted at 75°C during the reaction. Then, the initiator (KPS) was fed into the reactor to start the polymerization. The total reaction time was about 3 h. The solid content was measured gravimetrically as 18% (by weight).

**Synthesis of Comb Polycarboxylic Acid Surfactant**

The comb polycarboxylic acid (CPCA) surfactant has
been prepared from oligomeric unsaturated diols and acrylic acid (AA) by radical polymerization under specific conditions. Scheme I shows the synthesis scheme of comb polycarboxylic acid surfactant.

Chemical structure of comb polycarboxylic acid surfactant is composed of PAA blocks having COOH acid groups and grafted polyethylene oxide (PEO) chains as hydrophilic segments. The molecular weight of unsaturated diols was around 500. A 150 °C Waters gel permeation chromatography (GPC) (USA) method was used to measure the molecular weight. The OH value and acid value of CPCA were measured based on ASTM D4274-11 and ASTM D1639-90, respectively. The results are summarized in Table 1.

The protons of CH$_2$ group of grafted PEO segments in CPCA grafted copolymeric dispersant appeared at 3.6-3.7 ppm in $^1$H NMR spectrum. The protons of CH$_2$ group on the backbone belonging to oligodiols appeared at 2.9 ppm. The protons of CH and CH$_2$ on the PAA appeared at 2.5 ppm and 1.8 ppm, respectively.

**Synthesis of ZnS Nanoparticles**

To prepare ZnS nanoparticles via hydrothermal method, 1 mL of 2.7% w/v PS dispersion was diluted by 20 mL distilled water. An amount of 0.025 g PVP was added to the mixture to avoid aggregation during the reaction. An appropriate amount of surfactant was also added to the suspension under vigorous stirring, thereafter 0.878 g (0.004 mol) zinc acetate was introduced to the above-mentioned solution. Another solution was prepared by dissolving 0.601 g (0.008 mol) thioacetamide in 20 mL distilled water. The second solution was gradually added to the first one under stirring, and then the final solution was transferred into a 50-mL teflon-lined stainless steel...
autoclave. The hydrothermal reaction was carried out at 150°C for 4 h. Finally, the precipitated particles were removed and rinsed several times using centrifugation-resuspension in water and ethanol. Drying process was carried out for 24 h under vacuum at room temperature. Different samples which were prepared using 0, 0.55, 2.2 and 4.4 g/L surfactant contents were designated as ZPSH1 to ZPSH4, respectively (Table 2).

Characterization

Different powder samples were characterized by XRD using a Siemens D500 X-ray diffractometer (Germany) with CuKα radiation (λ = 1.54178 Å). The average crystallite size of ZnS particles was determined using Debye-Scherrer’s equation. The morphology and size of the resulting powders were investigated using scanning electron microscopy (SEM) (LEO 1455 VP, UK) and transmission electron microscopy (TEM) (Philips EM208S, The Netherlands) after dispersing the particles in ethanol. Infrared spectroscopy technique was used to characterize the structure of the obtained powder. FTIR Spectra were obtained by a Perkin-Elmer Spectrum in absorption mode. UV-Visible spectra were also collected by a Cecil UV-visible spectrophotometer (UK). Photoluminescence (PL) measurements were carried out on a Perkin-Elmer LS55 Fluorescence Spectrometer (USA). Particle size distribution was calculated by “Measurement Software” (Nahamin Pardazan Asia Co., Iran).

RESULTS AND DISCUSSION

Structural Analysis

Figure 1 shows the XRD patterns of ZnS particles in presence of different amounts of surfactant and the same amount of PS template synthesized at 150°C for 4 h. The patterns indicate the same single-phase cubic sphalerite (JCPDS card No.01-0792). No characteristic peaks of other phases are observed in diffraction patterns. The main peaks diffracted at 28.6°, 47.6° and 56.4° are assigned to (111), (220) and (311) planes of sphalerite crystal, respectively. The average crystallite size was determined by Debye-Scherrer’s equation:

\[ D = \frac{0.9\lambda}{\beta \cos\theta} \]

where λ is the wavelength of incident light, β is the full width at half of the maximum peak height (FWHM) in radians and θ is diffraction angle in degree.

The calculated mean crystallite size of different samples is summarized in Table 2. As it is evident from Figure 1 and Table 2, increasing the surfactant content suppresses and broadens the XRD peaks. It seems that the surfactant covers the PS surface and decreases the growth rate of sphalerite crystals. Therefore, reduction in the peak intensity and
crystallite size is due to the surfactant effect.

The effect of PS template on XRD patterns is also investigated. Figure 2 shows XRD patterns of the ZnS powder synthesized at 150°C for 4 h in presence of the equal amounts of surfactant (2.2 g/L) and different concentrations of PS. As shown in the figure, the products obtained with PS as template showed more intense peaks. It seems that the nucleation of ZnS begins on the surface of PS particles. In other words, formation of ZnS nanoparticles on the surface of PS template enhances the nucleation rate and subsequently augments the growth rate of ZnS nanoparticles.

**Microstructure Analysis**

Morphology and particle size of PS particles were characterized by SEM technique. Figure 3 shows monodispersed polystyrene nanoparticles with particle size distribution around 40-80 nm (Figure 3b). The decrease of PS particle size in the dispersion increases the number of ZnS nanoparticles. Thus, the synthesized ZnS nanoparticles formed a thin layer on the PS particles and produced less unabsorbed secondary particles [19].

The effect of surfactant content on the ZnS nanoparticles size and morphology was also investigated. The SEM images of ZnS nanoparticles synthesized hydrothermally at 150°C for 4 h using different surfactant contents are represented in Figures 4a, 4c, 4e and 4g. Moreover, particle size distribution charts of ZSPH1-4 are illustrated in Figures 4b, 4d and 4f, respectively. As seen in Figures 4a and 4b (sample ZPSH1), the absence of surfactant results in submicron-spheres with particle sizes in the range of 700-1000 nm. Qian et al. demonstrated that submicron-sphere ZnS particles are formed by the reaction of dissociated Zn2+ in the aqueous solution with S2- [23]. The rough surface of particles is resulted from the existence of primary particles [24]. Figures 4c and 4d correspond to ZPSH2 sample obtained at a low concentration of surfactant. It contains both de-agglomerated submicron-spheres and nanospheres with diameters in the range of 200-500 and 100-180 nm, respectively. Figures 4e and 4f show the ZPSH3 sample which was prepared with a medium amount of the surfactant. It is concluded that as the surfactant concentration increases, the number of submicron-particles and the size of nanospheres decrease to 100-140 nm. In ZPSH4 sample synthesized in the presence of the highest amount of surfactant (Figure 4g), hard agglomerates are formed. Agglomeration is mainly due to accumulation of surfactant micelles above critical micelle concentration (CMC point). Figure 5 illustrates the surface tension curve of solution versus different concentrations of CPC surfactant. Surface tension of solution decreases linearly up to 4300 mg/L. Above this value, further increase of surfactant content did not have appreciable influence on the surface tension. Therefore, the CMC point of CPC surfactant is about 4300 mg/L which is in good agreement with the morphological results.

Figure 6 shows the SEM micrographs of samples synthesized with and without PS template. Particle size distribution charts of the mentioned samples are illustrated in Figures 6b and 6d, respectively. ZnS

![Figure 3. (a) SEM Image of PS synthesized by emulsion polymerization and (b) particle size distribution curve of image.](image-url)
Figure 4. SEM Images of the ZnS powders synthesized at 150°C for 4 h using (a) 0 g/L, (c) 0.55 g/L, (e) 2.2 g/L and (g) 4.4 g/L surfactant contents, particle size distribution charts of (a-d) figures illustrate in Figures b, d and f, respectively.
Figure 5. Surface tension curve of solution versus concentration of CPCA surfactant.

nanoparticles deposited on the surface of PS template consists of partially uniform dispersed particles, whereas in the absence of the template, irregular particles are formed. Although, the average particle size increases from 100-120 nm to 120-140 nm with PS template, more uniform distribution is observed in Figure 6d.

Morphology, size and the structure of ZnS primary particles were also characterized by TEM. Figure 7 shows the TEM micrographs of ZPSH3 sample synthesized in presence of 2.2 g/L surfactant. As shown in the figure, the size of ZnS nanoparticles has reached 100 nm. TEM Images also show the raspberry-like morphology of nanoparticles. It is evident that the size of primary particles is in the range of 8-15 nm. This size is in good agreement with crystallite size determined by Debye-Scherrer’s equation (Table 2). The selected area in electron diffraction pattern of ZPSH3 sample is also shown in Figure 7. The formation of three rings related to (111), (220) and (311) planes of ZnS sphalerite phase is in agreement with XRD results.

Chemical Composition of Synthesized Samples

The FTIR spectroscopy of different components is illustrated in Figure 8. Since the absorption band of ZnS occurs below 440 cm⁻¹, no absorption band appears between 4000 and 500 cm⁻¹ for ZnS [25,26].
The broad absorption bands at 2915 and 3420 cm\(^{-1}\) are assigned to C-H and O-H bonds, respectively. The sharp band at 1643 cm\(^{-1}\) is assigned to C=O. It seems that C=O band at 1680 cm\(^{-1}\) of pure PVP are shifted to 1643 cm\(^{-1}\) in presence of ZnS particles. This wavenumber reduction arises from bond weakening via partial transfer of electron density of carbonyl oxygen to the Zn. The weak bands at 1000, 1278 and 1438 cm\(^{-1}\) can be assigned to C-N bond, N\(\equiv\)H-O complex and stretching of pyrrolidone carbonyl groups, respectively [27,28]. Weakening of PS absorption bands in different samples can be related to surface coverage by adsorbed PVP. A peak appearing at 1700 cm\(^{-1}\) with higher surfactant content (which is related to carbonyl group of the surfactant) should be due to total coverage of the particles by surfactant layers.

**Suggested Model for the Formation of ZnS Particles**

A schematic model for the formation of ZnS nanoparticles on the surface of PS template is also suggested in Scheme II. Zhang et al. showed that PVP stabilizes the particles through three steps: (1) formation of PVP-metal complex, (2) promotion of metal nucleation and (3) the steric stabilization of PVP [27]. It is believed that the formation of ZnS nanoparticles occurs in four steps: (1) PVP adsorption on the surface of PS which results in an increase in steric stabilization of PS nanoparticles, (2) coverage of PVP adsorbed-PS template surface by surfactant which prevents particles from agglomeration and reduces particle growth, (3) formation of coordination bonds between Zn\(^{2+}\) ions and PVP chains and (4) controlled nucleation and growth of ZnS nanoparticles by thioacetamide decomposition under hydrothermal conditions. In other words, PVP-Zn complex persuades ZnS particles to consist on the surface of PS template and the surfactant controls size and morphology of particles and primary particles by grafting on the surface of ZnS nanoparticles. This crystal growth mechanism is demonstrated by weakening of the PS peaks and intensification of the PVP and surfactant peaks in FTIR spectra.

**Optical Properties**

Optical properties of ZnS nanoparticles were studied using UV-visible and photoluminescence spectrophotometers. As shown in Figure 9a, by increasing the surfactant content, the absorption edge of ZnS samples undergoes some blue shift. A decrease in
particle size is responsible for the decline of maximum exciton absorption wavelength ($\lambda_{\text{max}}$). Consequently, blue shift of adsorption edges is due to the quantum confinement of the photogenerated electron-holes [29]. The sharp absorption peak around 200 nm is related to the PVP which was added for UV-visible analysis. Moreover, band gap values of ZnS nano-particles are also evaluated. Following relation determines the band gap of semiconductor:

$$ (\alpha h \nu)^2 = c(h \nu - E_g) $$  \hspace{1cm} (1)

where $\alpha$ is the adsorption coefficient, ($h \nu$) is the incident photon energy, C is a constant and $E_g$ is the band gap of particles. $\alpha$ Values at different wavelengths calculated by eqn (2):

$$ \alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) $$  \hspace{1cm} (2)

where $d$ is path length and $T$ is transmittance at different wavelengths ($\lambda$). $T$ Values are determined using absorbance (A) versus wavelength ($\lambda$) plot (Figure 9a). For calculating the band gap, values of ($\alpha h \nu$)$^2$ versus $h \nu$ is plotted [30]. By extrapolation of the straight portion of the graph on $h \nu$ at $\alpha = 0$, $E_g$ of ZnS nanoparticles is obtained. As shown in Figure 9b, $E_g$ (3.88 eV) determined by extrapolation is in good agreement with Figure 9a.

The PL spectrum of ZPSH3 sample excited at 368 nm is shown in Figure 10. The spectrum consists of two blue peaks at 400 and 425 nm which are related to electron-hole recombination from internal vacancies for zinc and sulphur atoms [31]. The splitting of blue peaks is due to surface defects energy in the ZnS nanoparticles [8].

**CONCLUSION**

ZnS particles were successfully synthesized via hydrothermal method. It was found that the size of nanoparticles under hydrothermal conditions is affected by the anionic surfactant concentration and PS dispersion. Primary particles are semi-separated and morphology of particles is raspberry-like. The size of ZnS primary particles were in the range of 8-15 nm. Absorption edge blue shift in UV-vis spectra in different samples could be attributed to quantum confinement. The emission peaks at 400 and 425 nm could be related to electron-hole recombination from internal vacancies of Zn and S atoms. Further studies on simultaneous effect of surfactant and PS revealed
that the surfactant inhibits crystal growth during hydrothermal conditions. Nevertheless, PS as a seed enhances the crystal nucleation and growth rate, but increases the uniformity of ZnS particles. Consequently, the presence of surfactant and poly-styrene simultaneously results in the formation of more uniform ZnS shell on the surface of PS nanoparticles.

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