OPTICAL, STRUCTURAL AND MORPHOLOGICAL STUDIES OF BEAN- LIKE ZnS NANOSTRUCTURES BY AQUEOUS CHEMICAL METHOD

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The ZnS semiconducting nanoparticles were synthesized by simple chemical reaction of $ZnCl_2$ and Na_2S in aqueous solution. The main advantage of this method is the use of non toxic precursors and water is used as solvent. The as-prepared ZnS nanoparticles have average size of 12 nm. The structural, morphological, chemical composition and optical properties of the nanoparticles have been investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), Ultra Violet Spectroscopy (UV) and Photoluminescence (PL).

1. Introduction

Nanosized inorganic semiconducting materials have been generating an extensive interest in recent years owing to their structure, chemical and physical properties, which are different from those of the bulk materials. ZnS has a wide band gap of 3.5 - 3.8 eV at room temperature and the band gap can be tuned in the UV region. It is an important inorganic material for a variety of applications including photoconductors, solar cells, field effect transistors, sensors, transducers optical coatings and light-emitting materials [1-4]. It has been investigated extensively, because of its potential optical applications [5-7]. ZnS doped with various transition metal ions such as manganese is an efficient light emitting material [8-10]. Nanostructured materials have been synthesized by many simple methods such as wet chemical method [11-12], solid-state reaction method [13], etc. The purpose of the present work is to synthesize ZnS nanoparticles using aqueous chemical method and investigate the properties such as size, structure, band gap, absorption and luminescence.

2. Experimental details

The synthesis of ZnS nanoparticles was carried out by aqueous chemical method using zinc chloride and sodium sulfide as source materials. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at low temperature and ambient conditions. In a typical preparation, solution of 1 M zinc chloride was prepared in 100 ml of deionized water and then the solution of 1 M sodium sulfide was added drop wise to the solution which was kept on stirring using a magnetic stirrer at 70 ^{0}C, which resulted in formation of ZnS nano colloid. The nanoparticles were collected by centrifugation at 2000 rpm for 15 minutes. And further purification was made by ultrasonic bath. The resultant product was finally dried at 120^{0}C for 2 hours.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZnS nanoparticles. It reveals the hexagonal structure for the as – prepared nanoparticles [14] and the features correspond to the (101), (002) and (110) planes, which show obvious size broadening effects, indicating the finite size of the nanoparticles.
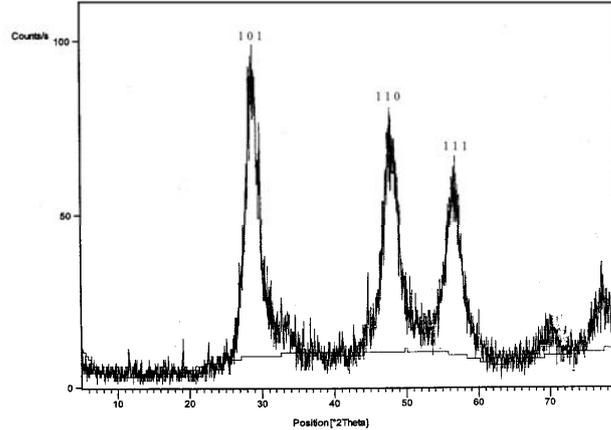

Fig. 1 XRD pattern of ZnS nanoparticles.

The average particle size from the most intense peak was estimated to be 12 nm using Debye- Scherrer formula [15].

$$D = k\lambda/\beta\cos\theta \tag{1}$$

where D is the mean grain size, k is a geometric factor, λ is the X-ray wavelength, β is the FWHM of diffraction peak and θ is the diffraction angle. The FWHM of the XRD peaks may also contain contributions from lattice strain. The average strain of the ZnS nanoparticles was calculated by Stokes – Wilson equation

$$\varepsilon_{str}= \beta/4\tan\theta \tag{2}$$

Lattice parameters 'a' and 'c' were calculated by the relation

$$d^2/a^2 = (h^2+k^2+l^2)$$
$$d^2/c^2 = (h^2+k^2+l^2) \tag{3}$$

The dislocation density was also calculated from the relation [16]

$$\delta = 15\varepsilon/aD \tag{4}$$

The average lattice strain and the dislocation density were estimated to be 2.80 x 10^{-3} and 3.39 x 10^{-15} lines/m.

Fig. 2. shows the SEM image of ZnS nanoparticles. The morphology of the ZnS resembles the bean-like nanostructure [12]. The FTIR spectrum for ZnS nanoparticles is presented in Fig.3.
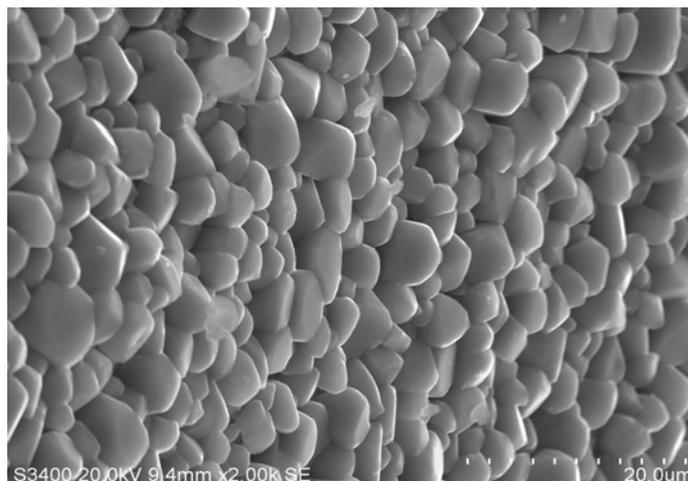
Fig. 2 SEM image of ZnS nanoparticles.

The spectrum in the range 300-4000 cm^{-1} was showing IR absorption due to the various vibrations involved. The major peaks are at 655.8 cm^{-1}, 997.1 cm^{-1}, 1413.7 cm^{-1}, 1633.6 cm^{-1} and 3342.4 cm^{-1}. In this spectrum, the two peaks observed correspond to O-H stretching (3342.4 cm^{-1}) and O-H bending (1633.6 cm^{-1}) of water [17].
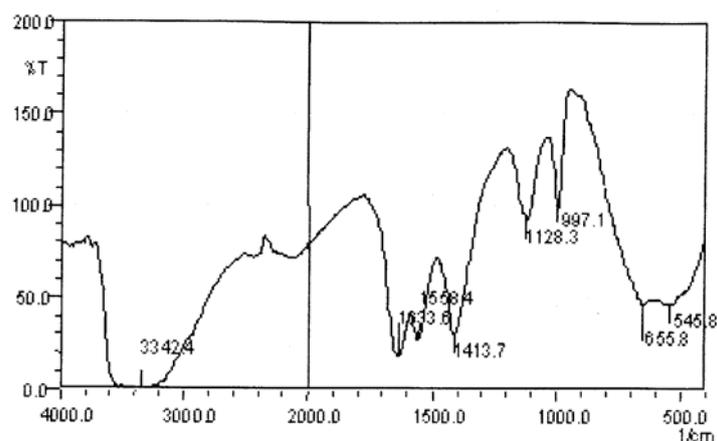
Fig. 3 FTIR spectrum of ZnS nanoparticles

The room temperature UV-Vis spectrum was recorded using Perkin Elmer Spectrophotometer in the absorption mode and is shown in Fig. 4. It exhibits the absorption edge of ZnS nanoparticles at 325 nm (3.8 eV), which is slightly blue shifted from that of bulk ZnS (340 nm, E_g = 3.65 eV). This closeness of the absorption peak to the bulk ZnS crystals are attributed to the near-band-edge free excitons [18]. The broadening of the absorption spectrum could be due to the quantum confinement of the nanoparticles.
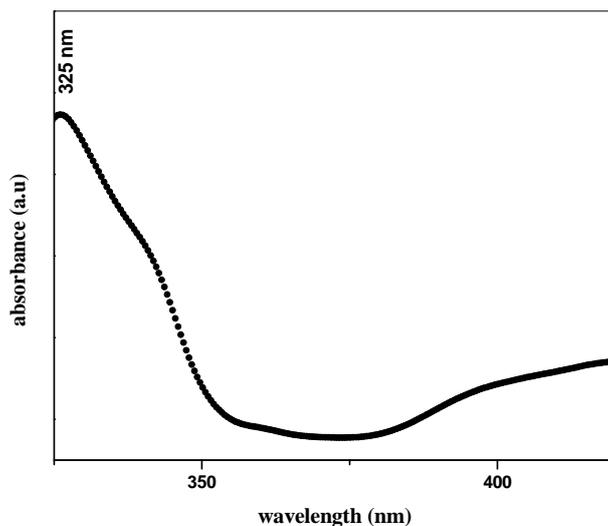
Fig. 4 UV Spectra of ZnS nanoparticles.

To investigate the luminescence properties, the PL spectra of the as-synthesized ZnS nanoparticles were performed. Fig. 5. Shows the emission spectra and from the data we can see the strong emission bands at about 388 nm and 398 nm. Usually for semiconductor nanocrystals, two emission peaks can be observed- the exciton and the trapped luminescence [19]. The exciton emission peak is sharp and the trapped emission is broad [20,21]. The emission bands showed in the spectra can be attributed to band gap emission and the strong band gap emission demonstrates the high crystalline nature of the as-synthesized particles.
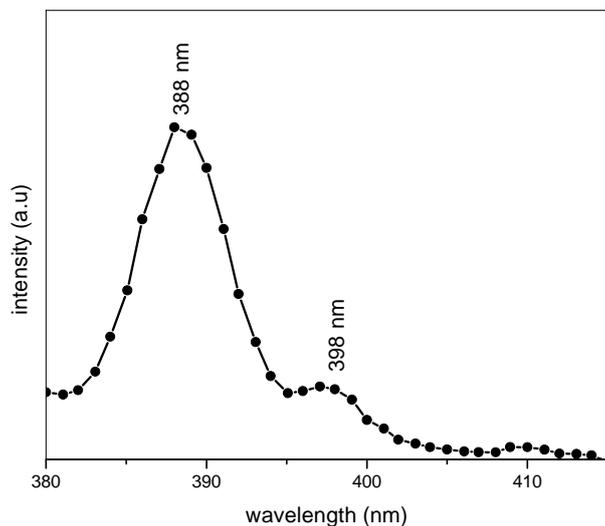

Fig. 5 The room temperature PL emission spectra of ZnS nanoparticles

4. Conclusions

In conclusion, we have successfully synthesized the bean-like ZnS nanostructures by a simple aqueous chemical method using pure aqueous route resulting in primary particle sizes of 12 nm. This particle size was calculated from the Debye- Scherrer formula. SEM image is used to study the morphology of the synthesized nanoparticles. FTIR spectra showed the possible stretching and bending modes of the ZnS. UV spectra revealed that the absorption band was blue shifted from the bulk. Photoluminescence investigation evidenced the high crystalline nature of the ZnS nanoparticles.

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