SYNTHESIS AND OPTICAL PROPERTIES OF AGGREGATED NANOSPHERES OF ZnS NANOPARTICLES

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Aggregated nanospheres of sizes ~ 100 nm of ZnS nanoparticles of diameters ~3 nm were synthesized by a chemical precipitation method using biomimetic approach in pepsin matrix at room temperature. The particle size was calculated as 2.74 nm from peak broadening of X-ray diffraction (XRD) pattern. The blue shift in the optical absorption spectra demonstrated the effect of strong quantum confinement in the ZnS nanocrystals. XRD studies of ZnS nanoparticles showed that the ZnS nanoparticles were of zinc blend structure. The purity and compositions of the prepared samples were studied by EDAX. The aggregation of ZnS nanoparticles to nanosphere was confirmed by TEM images.

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1. Introduction

The properties of semiconductor nanoparticles strongly depend on its size, shape, composition, crystallinity and structure [1]. It is a great challenge and striking aim to precisely control these parameters of nanoparticles for the synthetic chemists. However, the assembly of nanoparticles is a key step for their applications in micro- and nano-electronic devices [2-4], which is as important as the preparation of these nanosized particles. Therefore, the exposure of exact size and shape controlled synthesis of nanostructure materials is becoming a great challenge for the nanotechnologists. Recently, semiconductor nanoparticles have been extensively investigated and gained much interest due to their unique properties and applications in diverse areas of science and technology [5-9]. Because of their unique and size dependent properties arising from quantum confinement and surface effect, nanocrystals of ZnS have been extensively studied [10-15]. ZnS is an important II-VI group compound semiconductor with wide band gap energy of 3.68 eV, has attracted much research interest due to its potential applications in many solid state devices. Literature survey reveals that a large number of techniques for preparing ZnS nanoparticles have been applied by different workers [16-29]. Growing nanocrystals in a matrix is a way to have surface passivated nanoparticles, which are stabilized against environmental attacks. To create nanocrystals of the desired size and properties in a matrix, it is required that the growth parameters are properly tuned. To synthesize nanocrystals of ZnS in a matrix or in capping agents, many research groups have reported their research work [30-37].

Biological systems can control mineralization and synthesis of various nanocrystals in the exact shapes and sizes with high reproducibility and accuracy. Therefore, it is a logical approach to use to grow nanocrystals via biomineralization. Recently, biomimetic synthesis of inorganic nanocrystals has attracted more and more attention. Proteins are functional macromolecules distributed in living beings. Some proteins have a function called biomineralization to accumulate

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inorganic materials and form bone, shells or nanocrystals, which interest us in studying the function of the protein in biomimetic synthesis of ZnS nanocrystals. Pepsin is a kind of protein that present in large amounts in digestive juices and can be easily isolated.

In this paper, we have discussed the synthesis and optical properties of aggregated nanospheres of ZnS nanoparticles prepared in pepsin matrix. The optical properties of as synthesized ZnS nanocrystals were characterized by powder XRD patterns, optical absorption, TEM and EDX analyses.

2. Experimental betail

Aggregated nanospheres of ZnS nanoparticles stabilized in pepsin matrix were synthesized by colloidal precipitation method. The reagents zinc chloride ZnCl2, Thioacetamide (CH_3CSNH_2) Tris Buffer $NH_2C(CH_2OH)_3$ and pepsin were used as received without any further purification. Firstly 0.40 gm pepsin was dissolved in 180 ml distilled water in a flask. Then make 0.5 M solution of zinc chloride in distilled water in another flask. Now take 10 ml solution of 0.5 M zinc chloride and add it in first pepsin solution and stirred. Now make 0.5M solution of Tris Buffer ($NH_2C(CH_2OH)_3$ (0.62070 gm) in distilled water. Now add this solution slowly in the mix solution of zinc chloride and pepsin and stirred up to the pH becomes 7.0 and now we put this reaction till 24 hours. Now make 1M Thioacetamide (CH_3CSNH_2) (3.7565 gm) solution in distilled water and add it in above mix solution of zinc chloride and pepsin having 7.0 pH and stirred till 48 hours at room temperature. The slowly release of S^{2}– from thioacetamide led to the formation of ZnS nanocrystals. The resulting solution was centrifuged at 4000 rpm, and ZnS precipitate was obtained. After removal the supernatant, the remaining solid was repeatedly washed with distilled water and separated by centrifugation, then dried in vacuum.

3. Results and discussion

The reaction between Zn^{++} and S^{--} is very fast and induces ZnS aggregation quickly in aqueous solution. In order to slower the chemical reaction, we designed that Zn^{++} was coordinated by pepsin and S^{--} was supplied from thioacetamide. Thioacetamide is comparatively unstable in aqueous solution and slowly hydrolyzes to release S^{--} into the reaction solution.

3.1. X-ray diffraction patterns

X-ray diffraction patterns were used to determine the particle size ZnS nanocrystals by using Scherrer formula:

$$(t = k\lambda / B \cos \theta_B)$$

Where k is a constant taken to be 0.9, λ is the wavelength of X-ray used ($\lambda=1.54A^0$) and B is the full width at half maximum. Fig. 1 Shows the XRD pattern of ZnS nanocrystals prepared in pepsin matrix at room temperature.

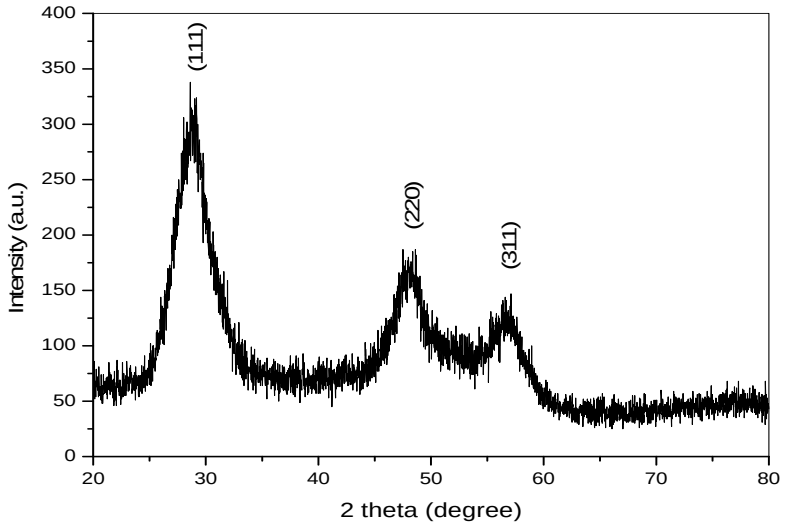


Fig. 1: XRD pattern of ZnS nanocrystals prepared in pensin matrix at room temperature.

From this figure it is clear that sample prepared at room temperature have a high degree of crystallographic orientation. The peak at $2\theta = 28.6^{o}$ is the characteristics of cubic (111) plane. The intensity of this peak is higher for the ZnS nano sample prepared at room temperature. From Fig. 1 average particle size has been calculated by using Scherrer formula and comes out as 2.744 nm.

3.2. Optical absorption:

Optical absorption spectra of ZnS sample were measured at room temperature using a HITACHI-U 3400 UV-Vis Spectrophotometer as shown in Fig. 2. It is clear from fig.2 that the sample exhibits absorption edge which is blue shifted with decreasing particle size and an evident of quantum confinement effect in the as-prepared ZnS nanoparticles. The absorption spectra of ZnS nanoparticles show a sharp absorption at about 265 nm and the absorption edge gave the band-gap value as 4.67 eV.

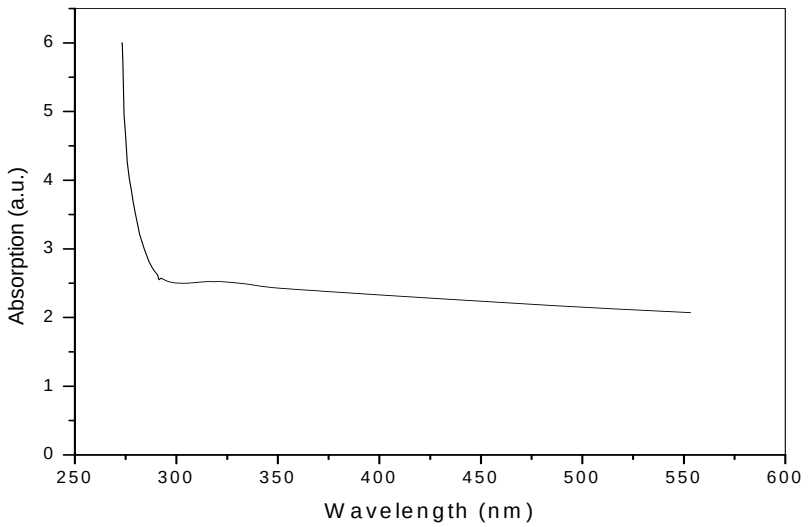
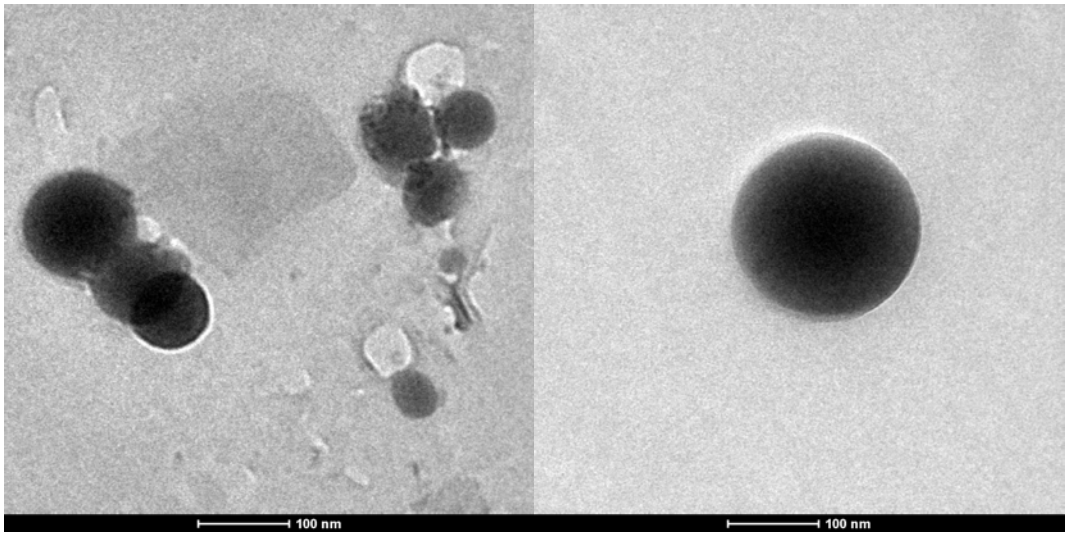


Fig. 2: Absorption spectra of ZnS nanocrystals.

3.3. Transmission electron microscopy (TEM):

Transmission electron microscopy image of the ZnS sample shown in fig 3 (a) clearly indicates aggregation of nanoparticles in form of nanospheres. Fig. 3 (b) shows the magnified TEM image of a single nanoshpere having diameter ~ 100nm. From this it is very clear that the nanospheres are composed of very small nanoparticles of ~ 3 nm sizes and is densely packed. The aggregation of the nanoparticles to nanospheres may be due to the solvent-pepsin interactions that may change its conformation and mobility in solution which results particle aggregation in form of nanospheres.



(a) (b)

Fig. 3. (a) TEM images of aggregation ZnS nanocrystals. (b) TEM image of single nanosphere.

3.4. EDAX Study:

The purity and composition of the prepared sample was studied by energy dispersive X- ray analysis (EDAX). A typical EDAX spectrum obtained from ZnS nanocrystals is shown in Figure 5, which exhibit the presence of Zn and S. The atomic percentage of Zn and S shows excess of Zn in the material.

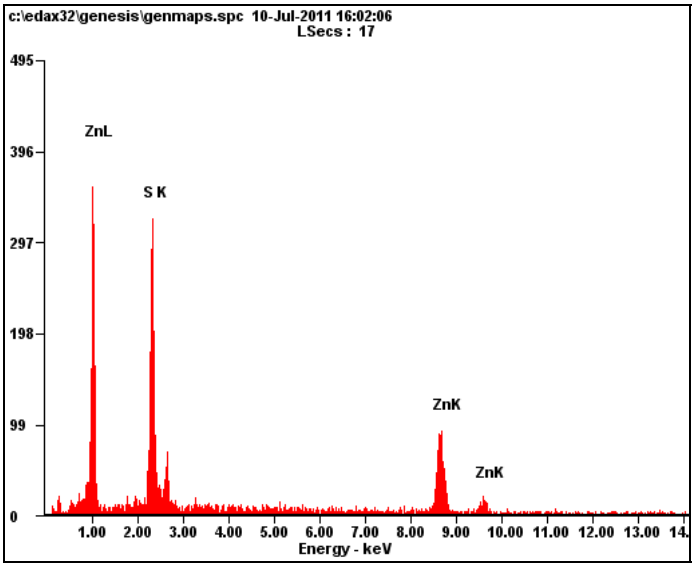


Fig. 4. EDAX spectrum of ZnS nanocrystals.

4. Conclusions

ZnS nanoparticles with sizes ~ 3 nm, which spontaneously aggregated to form nanospheres of ~ 100 nm diameter have been prepared by a chemical precipitation method using biomimetic approach in pepsin matrix at room temperature. The reaction between Zn^{++} and S^{--} is very fast and induces ZnS aggregation quickly in aqueous solution even in coordination by pepsin. The resulting ZnS nanocrystals have an average size 2.744 nm at room temperature as calculated by XRD patterns.

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