

Structural and Optical Properties of Chemically Synthesized ZnS Nanostructures

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Abstract—In the present work ZnS nanoparticles were synthesized by chemical co-precipitation method at room temperature. The structural properties of ZnS nanoparticles were determined by XRD (X-ray Diffraction), TEM (Tunneling Electron Microscopy) and their optical properties by UV-Visible and PL (Photoluminescence) analyses. XRD analysis showed that sample prepared were the cubic Zinc blende structure with particles' size in the ranges 5nm -12nm. The TEM analysis revealed the formation of ZnS nanoparticles with almost uniform shape and size. In optical characterization the UV_Visible spectra show a large blue shift. In PL analysis, three strong and board emission bands located at 365nm, 400nm and 425nm have been observed. It is well known that the luminescent peak centered at 365nm could be assigned to the UV-excitonic emission and other peaks attributing to the sulfur vacancy.

Index Terms—HRTEM, PL & quantum dots etc

I. INTRODUCTION

Semiconductor quantum dots based on luminescence properties of II-VI groups' elements have attracted special attention to research community due to their fascinating optical and electronic properties [1]-[5]. Synthesis and characterization of discrete nanostructures is of significant importance because of their fundamental role in basic research and technological applications [6]. Since nanostructures have a large surface to volume ratio, it exhibits enhanced surface and interface effects resulting novel phenomena. Therefore nanobuilding materials such as ZnO nanowires, Carbon nanotubes, ZnS nanopartilces, CdSe nanoparticles and GaN nanowires are intensively investigated for their practical applications [5]-[6].

ZnS is an important II-VI group semiconductor material with a direct band gap of 3.7eV and is widely used as phosphor in photoluminescence (PL), electroluminescence (EL) and optical sensor because of its better chemical stability as compared to other chalcogenides such as ZnSe [1]. It also exhibits wide optical transparency from the visible light (0.4 μ m) to the deep infrared region (12 μ m) which makes ZnS as one of the most promising luminescent materials among II-VI groups.

In this work, we have reported the spontaneous self-assembly of PVA (Poly-Vinyl Alcohol) stabilized ZnS nanopartilces into almost uniform and dense nanospheres of 10-15nm sizes. The morphological study of ZnS was carried out by XRD and TEM while its optical properties were

studied by UV-Visible and PL analyses.

II. MATERIALS AND METHODS

A. Synthesis

Zinc sulphide nanoparticles were grown on glass substrate as their films as well as colloidal nanoparticles through chemical co-precipitation techniques at room temperature [1]. Equivolume and equimolar (0.5M) solution of Zinc sulphate dehydrate and thiourea was prepared by dissolving in demonized water. The mixture of two salts were mixed with 3% solution of Poly-Vinyl Alcohol (PVA) and stirred. Ammonia was added to it until formation of clear metallic complex. The p^H was kept at 10-11. Then thiourea solution was allowed to mix with the neutral complex solution which yielded pure ZnS due to the chemical reaction bsetween Zn metallic complex and sulfur ions. Commercially available glass micro slides were rinsed through boiling in chromic acid and dried in air. These glass slides were dipped in the matrix solution for 48-56 hours to cast thin films.

B. Characterizations

These thin films were taken for XRD study and the solutions were used for optical as well as TEM studies. The structural investigation of ZnS was carried out using X-ray powder diffractometer (Model: Seifert XRD 3003T/T) with CuK α radiation ($\lambda = 0.15406$ nm) scanning 2 θ in the range 20⁰ -80⁰. The morphology of the nanoparticles were characterized by transmission electron microscope (TEM)[Model; JEOL, JEM-2100) operated with an acceleration potential of 200kV. UV-Visible absorptions of the samples were recorded using an automated spectrometer (Model: HITACI 113210) in the wavelength range 250nm -500nm. PL emission spectra were measured with excitation wavelength 325nm using AMINC BOWMAN series-2 luminescence spectrometer [Model: A 357].

III. RESULTS AND DISCUSSION

A. XRD Study

X-ray diffraction (XRD) patterns of the synthesized ZnS colloidal powders have been depicted in Fig. 1. The XRD traces shows that the prepared zinc sulphate are crystalline having zinc blende type structure. The cubic Zinc blende structure was confirmed from the agreement of 2 θ values with standard JCPDS file data. The most prominent peak is oriented in (200) direction along with the other reflections at (111) and (222) planes. The lattice strain developed among the crystallites is of the order of 10⁻³. ZnS prepared without capping agent shows poor crystallinity. However the

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crystallinity has been improved with clear peak broadening for the ZnS dispersed in PVA matrix. Selective absorption of polymer on various crystallographic planes of nanocrystals plays an important role in controlling the product morphologies. The average particle sizes were measured using Debye Scherer formula and were found to lie in the range 10nm – 23nm [9]. XRD characterization also shows a clear broadening with a (2θ) peak around 36.87 in ZnS nanoparticles attributing the formation of nanostructure.

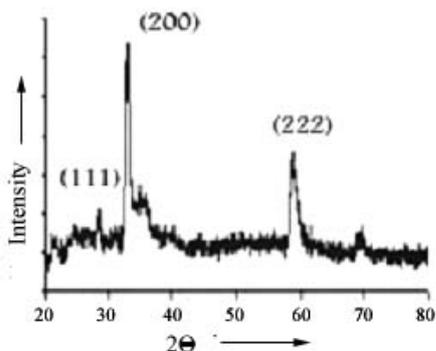


Fig. 1. XRD of ZnS

B. TEM Study

Morphology and structure of as-prepared ZnS nanoparticles were studied by the TEM analysis. Fig. 2(a) displays the TEM image of large number of assembled ZnS nanoparticles with almost uniform shape and size. It can be observed that the particles are of spherical shape with it size in the range of 5nm -12nm. The HRTEM image in Fig. 2(b) shows the ZnS nanopartilces are single crystalline. Fig.2(c).

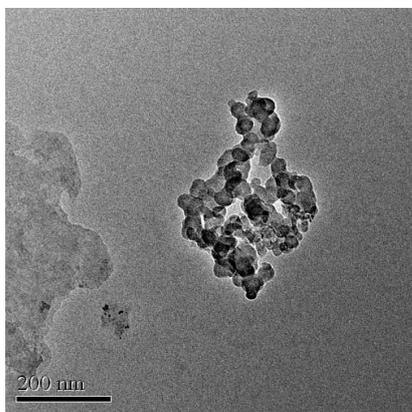


Fig. 2(a) TEM image of ZnS nanoparticles.



Fig. 2.(b) TEM image showing the diffraction pattern of ZnS nanostructure.

Illustrates the HRTEM image of corresponding nanostructures shown in Fig.2 (a) and the measured spacing of crystallographic plane is about 0.41nm [Fig.2 (d)].

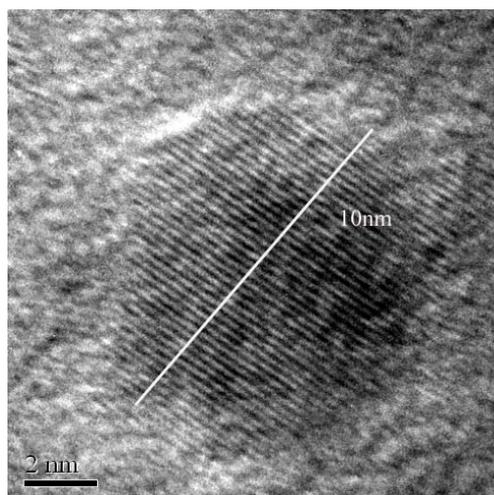


Fig. 2.(c) HRTEM showing the particles size of a single ZnS nanosphere.

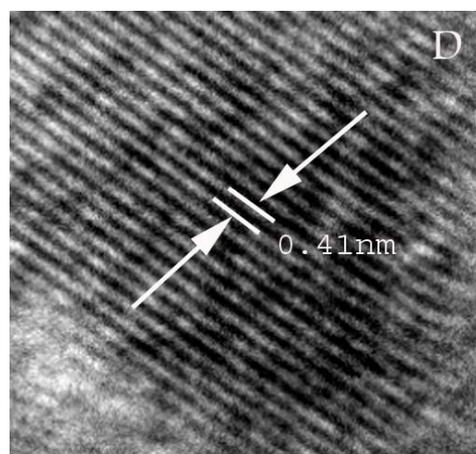


Fig. 2(d) HRTEM showing the lattice spacing of ZnS nanostructure.

C. UV_Visible Study

The UV_Visible spectra of the as-prepared ZnS nanopartilces are shown in the Fig. 3. It shows a strong absorption peak around 279nm which is large blue shifted from the bulk absorption at 315nm. This absorption peak due to the transition between the electronic state in the conduction band and whole state in the valance band is given in the Table. I. From the absorption peak the optical energy band gap of ZnS nanostructure has been calculated using the formula

$$E_{gn} = hv_{gn} = hc/\lambda_{gn} \tag{1}$$

where h=plank’s constant and E_{gn} = energy band gap of the semiconducting nanoparticles in the optical spectra and the calculated band gap energies are shown in the Table I.

TABLE I: ABSORPTION EDGE AND BAND ENERGY IN (ELECTRON VOLT) CALCULATED FROM UV-VIS MEASUREMENT

Sample	Molarity	Absorption edge, λ_a (nm)	band gap energy E_g (eV)	Average blue shift(eV)
ZnS	0.5	279.5	4.43	0.83

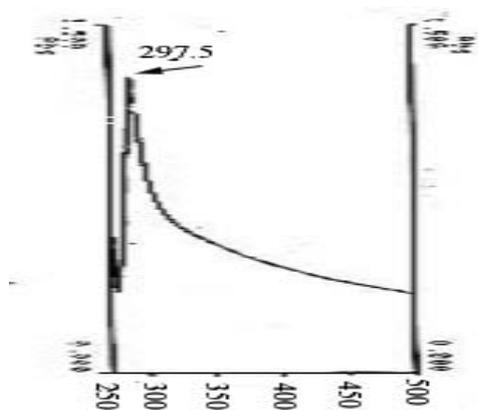


Fig. 3. UV-Vis absorption spectra of as-prepared ZnS nanoparticles.

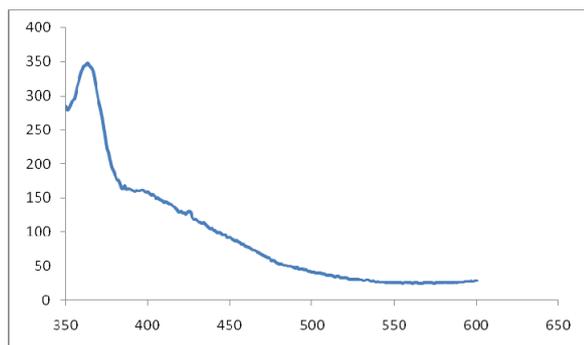


Fig. 4. PL spectra of as-prepared ZnS nanoparticles.

Average blue shift of 0.83eV is observed in the as-prepared ZnS nanostructure as compared to its bulk materials attributing the large optical properties changes.

D. PL Study

The room temperature PL spectra are recorded with 325nm excitation wavelength. Fig. 4 shows the PL spectra of band gaps located around 365nm, 400nm and 425nm. It is well known that the luminescent peak centered at 365nm could be assigned to the UV-excitonic emission.

The ZnS nanomaterials reported previously have PL emission with bands in the range 400-450nm associated with sulfur vacancy [1], [5], [4]. Further, the narrow emission bandwidth of the samples indicates a relatively narrow size distribution of the particles [10].

IV. CONCLUSION

The ZnS nanoparticles were successfully synthesized through chemical route and their structural as well as optical properties were investigated by XRD, TEM and PL. The particle sizes of ZnS nanoparticles as determined from XRD and TEM image are in good agreement. The UV-Visible spectra show a large blue shift attributing the enhanced optical properties changes. PL measurement shows Zn as well as Sulfur vacancy resulting some crystal defects.

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