

Structural and Optical Properties of Flower like ZnS Nanostructure

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Abstract: In the present work Flower like ZnS nanostructure have been grown on glass substrate by chemical bath deposition (CBD) method at room temperature. The XRD patterns of the specimen revealed the formation the cubic zinc blende structure of the ZnS nanoflower incorporated with some impurity of ZnO. The compositional analyses and structural morphology investigated by SEM, EDS and TEM confirmed the formation of Flower like ZnS nanostructure. The UV-visible absorption spectra show a large blue shifted that increase the band gap energy. The PL spectra of the as-prepared sample on deconvolution exhibit a strong emission centred at 358 nm corresponding to band gap energy of ZnS and other peak at 453nm correspond to the defect energy.

Index Terms - ZnS, PVA, SAED, HRTEM etc.

I. INTRODUCTION

Semiconductor nanostructures exhibit a variety of novel properties based on their size, composition and structural morphology [1]. ZnS has a band gap of 3.6 eV at 300K[2] and it is largely used as phosphor materials for the application in different light emitting devices and displays [3]. It is also emerged as most promising material for the application in different light emitting devices and displays [3]. The spectra reveal a strong emission centred at 358 nm corresponding to band gap energy of ZnS while the peak at 453 nm correspond to the defect energy. The use in optical coatings, solid-state solar window layers, photo-conductors, optical sensors and other non-linear optical devices. The structure of ZnS is mostly found either in cubic sphalerite or hexagonal wurtzite type form [1-3]. However, mixed type structures comprising both structural forms are also reported. [4]. The anisotropic growth in ZnS is attributed to the difference of surface energy of different crystallographic planes. Another aspect is the surface polarity and chemical activities [3-4]. The positively charged Zn and negatively charged S polar surfaces in ZnS result normal dipole moment and spontaneous polarization along the c-axis as well as surface energy [6]. The chemical activities of the Zn-terminated surface are very active and thereby it is easier to initiate a new nanostructure onto it whereas the S-terminated surface is relatively inert [4].

ZnS shows novel nanostructures depending upon the quantum confinement along zero, one, two and three dimension. A variety of ZnS nanostructures are reported by various workers as in the form quantum dots [3,5], nanorods [4], nanowires [5], nanobelts [6], nanoribbon [7], nanocomb [8], nanohelices [9], nanoflakes [10], nanosaws [11], and even nanoflowers [12]. Nanoflowers offer high surface area for dye-sensitized solar application. These newer nanostructures exhibit their potential to be used in spintronics, photonics and many other fields.

Several synthesis methods like PVD (Physical Vapour Deposition) [4], Thermal Evaporation Method [13], Close Spaced Evaporation (CSE) Technique [14], Chemical Bath Deposition (CBD) Method [5], Lithography [15], Solvothermal Method [25] etc. are adopted to grow these nanostructures. However in case of chemical synthesis of ZnS, the oxidation problem is quite prominent and that may result the final product as ZnS_xO_{1-x} or the mixture of ZnS, Zn(OH)₂ and ZnO [17, 18]. ZnO possesses flowerlike structure upon oxidation in air. Hence a compositional study in case of chemically synthesized ZnS is quite essential. Keeping in view of above aspects, an experimental study to grow the ZnS nanostructures from the chemical reaction of aqueous solutions (in air) for large duration has been made. In the present work the formation of nanoflowers type ZnS nanostructures are reported. Special emphasis has been made to know the growth mechanism taking into account of oxygen incorporation.

II. EXPERIMENTAL:

Synthesis

Zinc sulphide nanoparticles were grown on glass substrate as their films as well as colloidal particles through chemical bath deposition (CBD) techniques at room temperature [5]. 3% Poly-Vinyl Alcohol (PVA) dissolved in de-ionised water was used as capping agent [18]. Ammonia was added to it until formation of clear metallic complex. The pH was kept in the range of 9-11. Then thiourea solution was allowed to mix with the neutral complex solution which yield pure ZnS due to the chemical reaction between Zn metallic complex and sulfur ions [5]. The glass substrates were cleaned and dried with a synthesis of procedure prior to deposition and dipped into the final matrix solution to cast films.

Characterization

The structure of the as-prepared ZnS was investigated using X-ray powder diffractometer (Model: Seifert XRD 3003 T/T) with CuK_α radiation ($\lambda = 0.15406 \text{ nm}$) scanning 2θ in the range 20° - 80° . Microstructure was studied with Scanning Electron Microscope (SEM) [Model: LEO 1430VP] operated with an acceleration potential of 15kV to 20 kV. The morphology of the nanoparticles were characterized by transmission electron microscope (TEM) [Model: JEOL JEM 100CX-II] operated with an acceleration potential of 100 kV. The UV-Vis absorption of the specimen was recorded using an automated spectrometer (Model: HITACHI 113210) in the wavelength range 200nm -800nm. PL emission spectra were measured with excitation wavelength 325nm using AMINC BOWMAN series-2 luminescence spectrometer [Model: A 357] [19].

III. RESULTS AND DISCUSSION:

Structural Studies

The X-ray diffractogram (XRD) patterns of as prepared ZnS colloidal powders have been depicted in Fig. 1. The XRD traces show that the prepared Zinc sulphate is polycrystalline having Zinc blende type structure [4]. The cubic Zinc blende structure was confirmed from the agreement of 2θ values with standard JCPDS Card no 80-0020 [20]. The most prominent peak is oriented in (200) direction along with the other reflections at (111), (220) and (311) planes. The average lattice constant calculated for cubic phase is found to be 5.41 Å which is close to the bulk value 5.43 Å. A small deviation however indicates that ZnS contains some inherent defects in the form of Zn interstitials or S^{2-} vacancies [19]. The average particle sizes are measured using Debye Scherrer formula ($d = 0.9\lambda/\beta\cos\theta$) and those are found to be 9.7 nm [21]

XRD characterization also shows a clear broadening with a peak around 33° . This is attributed to the presence of dominated (101) orientation of ZnO due to oxidation that usually occurs because of abundance of dissolved oxygen in the precursor solution as well as atmospheric oxygen [19]. During chemical reaction hours atmospheric temperature some Zinc atom directly oxidizes to form ZnO or/and some synthesized ZnS seed converted to ZnO on oxidation. The formation of ZnO on ZnS oxidation (especially at high temperature) is reported by several workers [17] that exhibits a broad peak along (002), (101) orientations. A close observation on the XRD traces reveals that the other peaks of ZnO corresponding to (002), (101), (102), (103) planes are also exit.

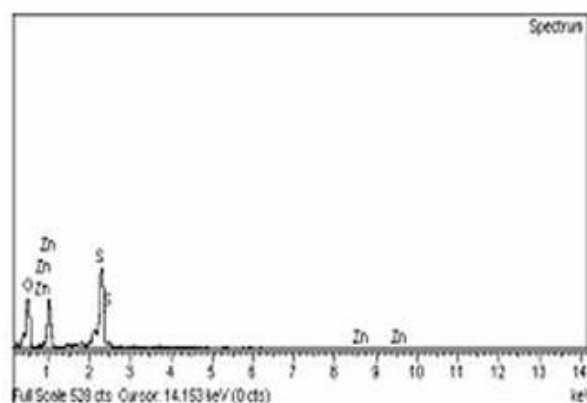
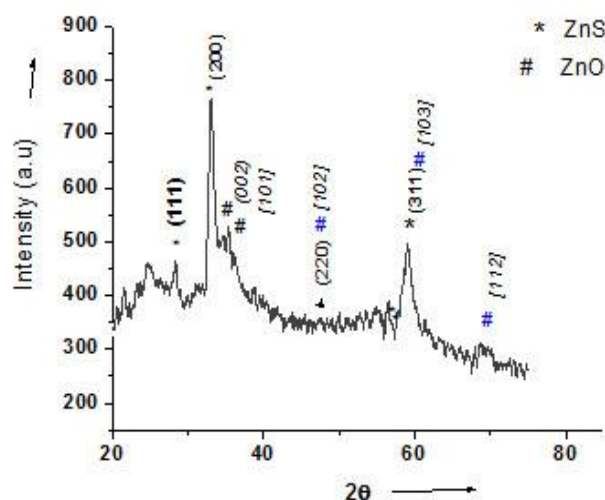


FIG. 1 XRD PATTERN OF ZnS NANOSTRUCTURE

FIG.2 EDS PATTERN OF ZnS NANOSTRUCTURE

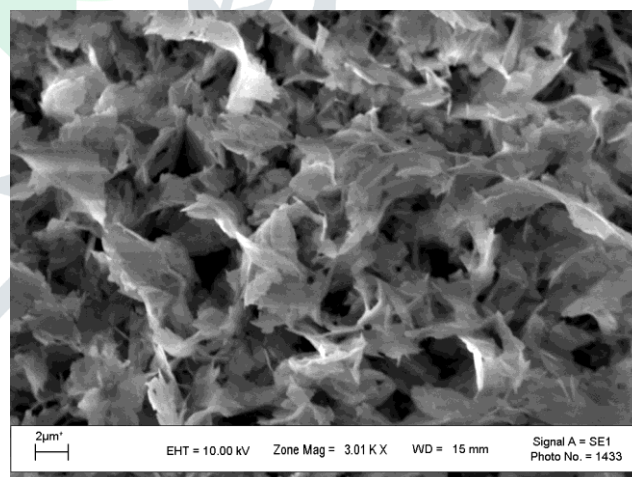
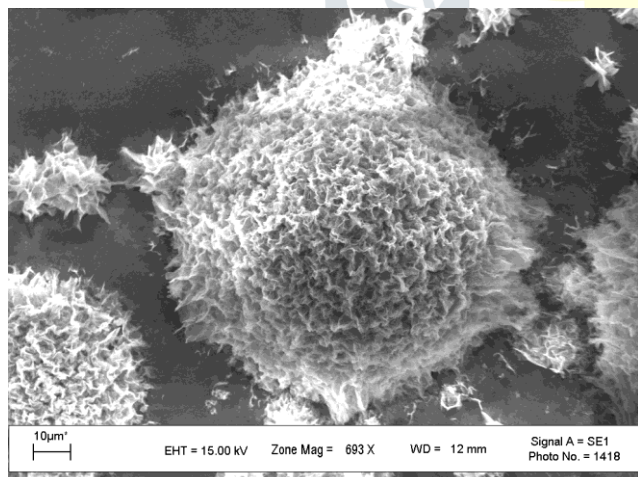


FIG. 3(A) SEM IMAGE FLOWER LIKE ZnS

FIG. 3(B) SEM IMAGE SELECTED AREA OF ZnS NANOSTRUCTURE

ZnO phase appeared is of hexagonal wurtzite type. However the (002), (220), and (311) planes of ZnS are expected to overlap (002), (102), and (103) planes of ZnO respectively. Similar XRD overlapping of cubic ZnS and wurtzite ZnO are also reported by Fei Li *et al* for chemically synthesized ZnO/ZnS microstructures [22].

The Figure 3(A) represents the SEM image of ZnS nanostructure which vividly shows the formation of flower like nanostructure. The Fig- 2(b) shows the selected area of the ZnS nanostructure with higher magnification. The Fig. (B) clearly exhibits the self-assembled well defined nanoflake structures [11]. Hence it may be inferred that the flower like ZnS nanostructure were due to the particular centre oriented self-assembly of the nanoflake like structure. Moreover a close observation on the nanoflower [Fig 2(a)] reveals that it consists of hexagonal nanopores made of those nanoflakes.

The EDS shown in the Fig.-2 indicates that the defect of Sulfur increases the incorporation of oxygen. In the present study the increase of oxygen incorporation is corresponding decrease of sulfur found from EDS analyses. It is inferred that oxygen incorporation can have ability to change the shape morphology of nanostructures in ZnS[13].

The TEM images of another ZnS is represented in Fig.3 It exhibit nanoflake like structures in consistent with the formation of flowerlike structures as observed in SEM investigation [Fig 3(B)]. A bundle of nanoflakes or tips are originated from single point self assembled spring type arranged to form a flower like structure . Different types of flower like structures of ZnO are produced depending upon different growth conditions. [6, 8,] The oxygen play an important role in the formation of such structure. ZnO nanostructure that possesses one dimensional growth like nanorods initially turns to flowerlike architecture when the growth time is in excess to several hours . During the preparation of ZnS films the oxygen is always found close to the substrate and in the near surface film layer . Hence it form oxide phase (ZnO) together with ZnS because of oxidation

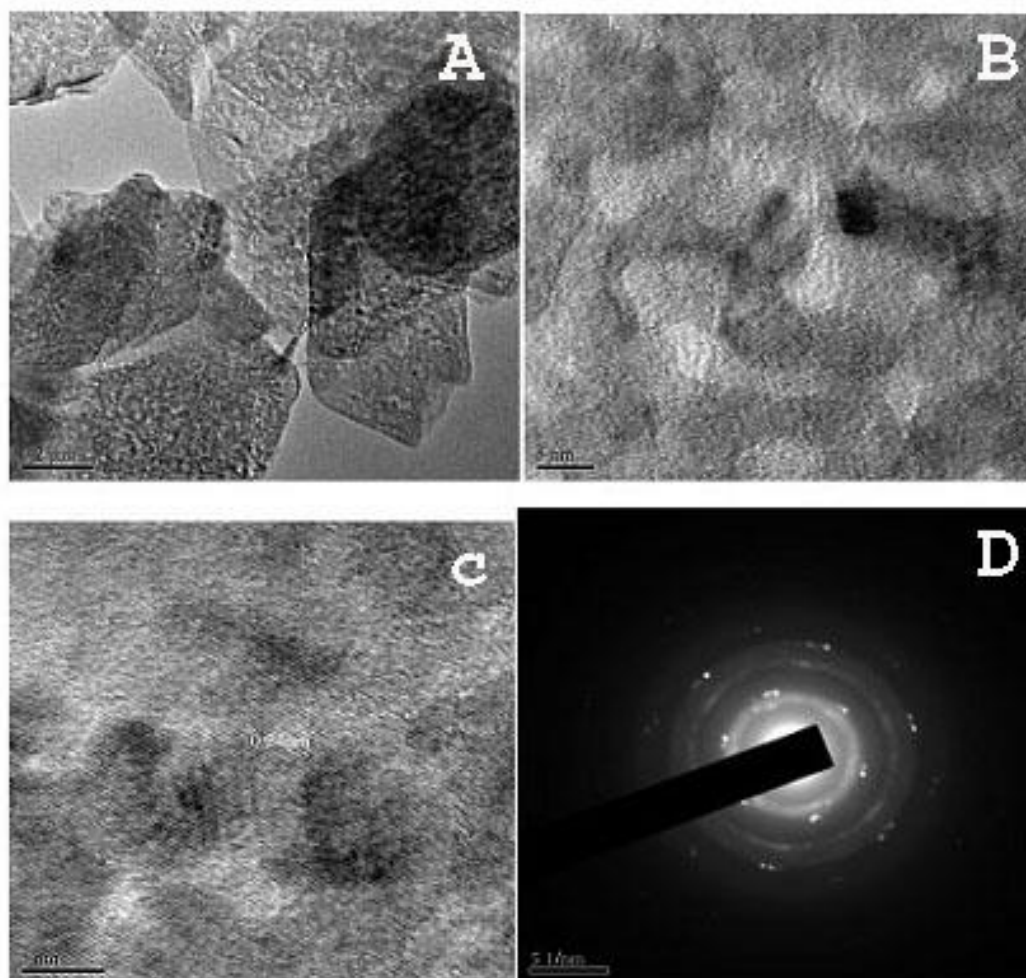
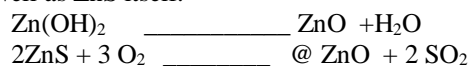


FIG. 4 (A) & (B) TEM IMAGE OF ZnS NANOFLOWER, 4(C) HRTEM and 4(D) SAED PATTERN OF ZnS NANOFLOWER

In vacuum condensed ZnS films, the amount oxygen to reaction is usually less than 1-2%. In chemical deposition process, the dominance of oxidation is more as the dissolved oxygen in the matrix solution is nearly 3-8% .In the present work as the deposition time is extended to several days [8-10]. Therefore the oxygen is expected to form oxide phase from oxidation of Zn(OH)₂ as well as ZnS itself.



The presence of oxygen in the as-prepared sample are confirmed from the EDS analysis as shown in the Fig. 2 . Oxygen incorporation may initiate for the growth of nanoflakes in ZnS prepared in water matrix. Although PVA acts as stabilizing agents for the growth of ZnS nanoparticles there exit a large concentration of S²⁻ ions at the surface with unsatisfied co-ordination which lead to high surface free-energy for the nanoparticles. These nanoparticles have tendency to reduce the excess surface energy through particle to particle attachment at the coherent interface [6, 9]. As the deposition time is quite large enough, oxygen incorporation is expected to play a role in free surface energy reduction mechanism. Atmospheric oxygen may react directly with S²⁻ to evolve SO₂ along with the formation of ZnO at the surface of nanoparticles..

This surface energy reduction mechanism leads to an antistrophic growth of nanoparticles and thereby the particles self assemble to give a shape and structural morphology. Since ZnO is distributed over the ZnS surface the synthesized ZnS may be called as partially ZnO centered nanoparticles. As ZnO on ZnS oxidation usually gives flowerlike structure, this plane is likely to initiate the formation of nanoflakes as well as nanoflower in the present work .

The High Resolution TEM images taken from the nanoflake are shown in the Fig. 4(C). The observed lattice spacing is 0.24nm which is equal to the distance between two planes in zinc blende structure ZnS. The selected area diffraction (SAED) of the nanoflakes shown in the Fig. 4(D) displays a spotted pattern and a set of rings of diffraction patterns. The spotted patterns corresponds to diffraction of ZnO with (211) zone axis[23].

Optical Properties

The UV-VIS spectra of the specimen are shown in the Fig. 5. It shows a strong UV-absorption around 288nm which is large blue shifted from the bulk absorption at 315nm [6]. Blue shift indicates the quantum confinement that increases the band gap upto 4.3eV. The spectra also exhibit an additional absorption at around 390nm corresponding to energy 3.18eV. This additional peak is attributed due to the excitonic transition of ZnO present in the nanostructures. Further a typical plot of $(\alpha h\nu)^2$ versus photon energy, obtained from the figure 5 is shown in the intersect of the Fig.-6 for the ZnS. The band gap observed in the plotted graphs is 4.3 eV which is more than the that of the bulk ZnS 3.6eV[24]

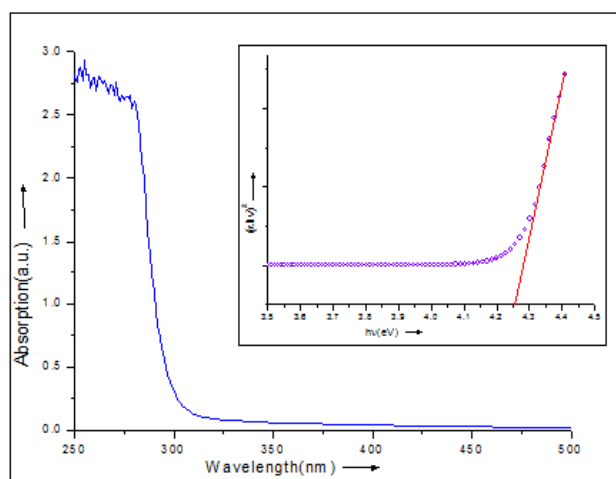


Fig.5 UV spectra of ZnS Nanoflower

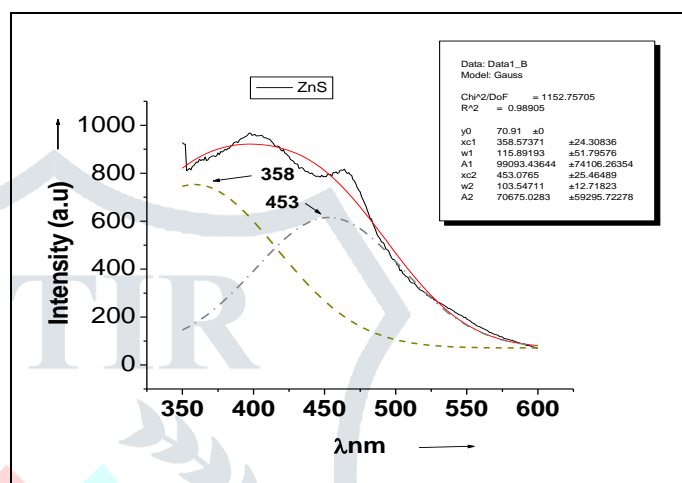


Fig.6 PL spectra of ZnS Nanoflower

The Figure-6 represents the PL spectra of the specimen recorded with an excitation wavelength of 325nm [6]. The PL spectra on deconvolution reveal a strong emission centered at 358 nm corresponding to band gap energy of ZnS while the peak at 453 nm correspond to the defect energy [6]. This defect energy may be attributed due to the hole traps originating from the unsaturated sp^3 orbital of the surface S^{2-} atom [16]. This visible emission may originate from self-activated centres. Vacancy states of sulfur species on the surface or interstitial associated with the peculiar nanostructure [25]. Keeping in view of above characterization it can be inferred that oxygen incorporation during chemical synthesis of ZnS is unavoidable at normal room temperature and pressure. Atmospheric oxygen and dissolved oxygen in precursor solution makes oxidation and convert ZnS particles partially or fully into ZnO under different conditions.

IV. CONCLUSION

In Conclusion, flower like ZnS nanostructures were successfully synthesized at room temperature by CBD technique. The Growth mechanism of the ZnS nanostructure was thoroughly studied by XRD, SEM and TEM, The XRD measurement established the formation the cubic zinc blende structure of the as-prepared ZnS nanostructure incorporated with some impurity of ZnO. The observed PL spectra revealed a strong emission centered at 358 nm corresponding to band gap energy of ZnS while the peak at 453 nm correspond to the defect energy. The UV-visible absorption spectra show a large blue shift that increase the band gap energy. This increased in band gap energy could be explored for the potential applications in the varieties of optoelectronic and light emitting devices.

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