ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF PVA-ENCAPSULATED ZNS NANOPARTICLES

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DOI: 10.5281/zenodo.50436

ABSTRACT

A systematic study is presented on the synthesis of PVA capped ZnS nanoparticles by using precursor solution of ZnCl2 and Na2S by a simple chemical precipitation method and characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV-visible absorption spectroscopy and impedance spectroscopy. The XRD patterns confirm formation of wurtzite hexagonal phase of ZnS with size ranging 2 to 6 nm. TEM studies have shown decrease in particle size with improve morphology on capping of PVA in ZnS lattice and Optical absorption spectra of synthesized material reveal blue shift in the optical band gap confirm quantum confinement effect of ZnS powder. Enhancement of conductivity in PVA- capped ZnS nanoparticles have been obtained from impedance measurements at different temperatures and suitably correlated to Davis- Mott model.

KEYWORD:. ZnS nanoparticles, quantum dots, PVA capping, optical band gap, electrical property.

INTRODUCTION

Semiconductor nanoparticles have attracted great deal of interest due to their novel size-tunable properties and consequently, in potential applications as optoelectronic devices and biomedical tags [1-4]. A route to derive new properties is to synthesize a semiconductor in nanometer sized entities. It gives rise to uniquely tunable properties from the quantum confinement of excited electron-hole pairs by the crystallite boundary [4-6]. Among the different group of semiconductor, II-VI group of semiconductors are reckoned as novel materials for development of optoelectronic devices owing to their tunable optical and electrical properties. Among the different members of this group, ZnS has been extensively investigated as it has numerous applications to its credit [7-10]. After the emergence of nanotechnology nanocrystallites of ZnS have acquired much significance as one can obtain desirable physical property by controlling the size, morphology, and crystallinity of nanocrystals. The size dependence of the bandgap is the most identified aspect of quantum confinement in semiconductors; the bandgap increases as the size of the particles decreases. When the dimensions of nanocrystalline particles approach the exciton Bohr radius, a blue shift in energy is observed due to the quantum confinement phenomenon. The effective mass model is commonly used to study the size dependent optical properties of quantum dots (QD) system. The tunability of the properties of nanoparticles by controlling their size may provide an advantage in formulating new composite materials with optimized properties for various applications. However, applications would be restricted due to different nonradiative relaxations pathways. One of the most important nanoradiative pathways is surface related defects. To overcome the above mentioned difficulties, organic and inorganic capping agents were used to passivate the free quantum dots. To control the growth of the nanoparticles, organic stabilizers (polymers) e.g. polyethylene oxide (PEO), poly(N-vinyl-2 Pyrrolidone, PVP), polyvinylcarbazole (PVK) are added during the wet-chemical synthesis for capping the surface of the particles [11–13]. To understanding the effect of capping on nanoparticles is one of the most important topics now-a-day. The fundamental question that we are attempting to address in this paper is how the capping causes any noticeable improvement of efficiency of nanoparticles. In view of the above, the present investigation an attempt have been made to systematic study on the effect of PVA encapsulation to the synthesis of ZnS nanoparticles and studying its structural and electrical properties.

EXPERIMENTAL

Synthesis

The ZnS Nanoparticle has been prepared at room temperature with using PVA as a capping agent via simple wet-chemical precipitation method. The starting materials used in the synthesis for ZnS nanostructures were Zinc (II) Chloride ($ZnCl_2$), Sodium Sulfide (Na_2S) fused flakes and polyvinyl alcohol (PVA). The chemical used in the synthesis were of analytical grade (AR) and used without any further purification. For the synthesis aqueous solutions of $ZnCl_2$, and Na_2S fused flakes with equal molar ratios and 1 molar wt% of PVA from these two salts were taken and admixed together drop wise under constant stirring at 700 rpm for reaction to proceed. The stirring was continued for 60 min at room temperature to achieve a homogeneous mixing. Subsequently, precipitate was filtered out and rinsed with distilled water several times to remove the impurities. Finally the products were allowed to dry up in an electrical oven at 150℃ for 10hour. The dried samples were allowed to cool down naturally at room temperature and grinded in an agate mortar to obtain ZnS nanopowder.

Characterization

The crystallographic phases of ZnS nanopowder were analyzed using X-ray (XRD) diffractogram taken from Shimadzu (model XRD 6100) with CuKα radiation (λ=1.54060Å). TEM images of nanoparticles were recorded using JEOL make transmission electron microscopy (model JEM 100). Optical band gap spectra and particle size of as synthesized samples were estimated from optical measurements conducted with the help of Systronics make UV-Visible spectrophotometer (model 2203) in 200nm-1100nm wavelength range. Electrical characterization of as synthesized ZnS samples characterized by LCR meter (Hioki Japan 3520) in the frequency range (40Hz- 100Hz) and temperature range (30ºC-90ºC).

RESULTS AND DISCUSSIONS

Structural Analysis

Fig 1 shows the XRD pattern of as synthesized ZnS powder and PVA capped ZnS powder in the scan range 20-75°. The XRD diffraction patterns of uncapped and PVA-capped ZnS sample powder exhibit diffraction peaks at 2θ positions of 28.62°, 47.8°, 56.67° corresponding to the (002), (110) and (112) planes, respectively matching closely with JCPDS card no. 75-1534. These observed diffraction peaks matches very well for wurtzite hexagonal phase of ZnS crystals for their intensity and peak position. The XRD peaks are broadened due to nanocrystalline nature of the synthesized samples. The crystallite size corresponding to the observed ZnS samples peaks have been calculated using Debye- Scherer relation [14]

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad \text{..... (1)}$$

where, λ is = wave length (Å) of the X-ray used, β= full width at half maximum (FWHM) in radians, θ = Bragg angle, D = mean size of crystallites. The estimated crystallites size of the synthesize ZnS Nanocrystallites has been tabulated in table 1. From the table it is apparent found that the crystallites size of the synthesized ZnS decreases with the capping of PVA.

TEM Studies

Fig 2 shows TEM micrographs for as synthesized and PVA capped ZnS samples. From as synthesized ZnS sample (fig 2a) shows crystalline aggregates of ZnS, which are made from uniform, fine and spherical particles with the diameter in the range 4 to 8 nm. The morphology of as synthesized ZnS provides look like aggregations consisting of ultrafine particles and they represent weak crystallinity. From PVA capped ZnS nanoparticles shows (fig 2b) spherical morphology of diameter ranging from 2 to 6 nm, particle size is very much reduced in addition, some lose sphere were also formed by aggregation of small particles. It is evident from TEM images that ZnS particle shows nanocrystalline structure and particles size decreases with capping of PVA supporting XRD data.

OPTICAL STUDIES (UV-VISIBLE ABSORPTION STUDY)

Measurement of the optical absorption characteristics of ZnS nanoparticles was performed by first dispersing a very small amount of the powder in distilled water, contained in quartz cavetti. Absorption characteristics of samples

were obtained by measuring the Absorbance (A) at different wavelength (λ) and there after calculating the absorption coefficient (α) at corresponding wavelengths using well known Beer-Lambert's relation:

$$\alpha = \frac{2.303\ A}{d} \text{ ---------- (2)}$$

where d is the path length. The incident photon energy (hν), absorption coefficient (α) and bandgap (Eg) of the material are inter related by the well known Tauc relation.

$$(\alpha h\nu) = K(h\nu - E_g)^n \text{ ------(3)}$$

where K is the edge width parameter, n depends on the type of transition, i.e. allowed direct, allowed indirect, forbidden direct and forbidden indirect for which it can have value of ½, 2, 3/2, and 3 respectively. The direct band gap value of ZnS nanoparticles was determined by plotting a graph between $(\alpha h\nu)^2$ versus hν as shown in fig.3. The optical band gaps was estimated by extrapolating the straight line portion of the graph (showing the maximum transmission, i.e. α = 0) on the hν axis. The energy band gap has been shown in table 1. Fig 3 shows that band gap of ZnS nanoparticles increases with PVA capping. This blue shift of band gap takes place essentially due to quantum confinement effect. The change in band gap can be correlated to the size of nanoparticles using the effective mass model which is used to study the size dependent optical properties of quantum dots (QDs) system. According to this model [15-17]

$$E_{g(nano)} = E_{g(\text{bulk})} + \frac{h^2}{8R^2}\left(\frac{1}{m_h^*} + \frac{1}{m_e^*}\right) - \frac{1.8e^2}{4\pi R\varepsilon_r\varepsilon_0} \text{ .... (4)}$$

where *h* is the Planck's constant, *R* the radius of nanoparticles. ε_r the dielectric constant of the material, and m_e^*, m_h^* are the effective mass of electron and hole. The second term involves the confinement effect while the third term results from coulomb interaction. The effect of third term is extremely small in case of nanoparticles and hence neglected for calculations. The particle size calculated using above model is also listed in table 1 along with the particle size extracted from XRD measurements. These values confirm the nanometric dimension of ZnS particles synthesized in the present investigation.

ELECTRICAL CHARACTERIZATION

Electrical conductivity behaviour of uncapped and PVA-capped ZnS nanoparticles have been described by well known Davis Mott model which has suggests two transport mechanisms described by separate activation energies [18-19]. According to this model, the behaviour of electronic conduction in disordered and non-metallic materials is controlled by the thermally assisted hopping of electrons between localized states near randomly distributed traps and in this case conductivity $\sigma_{DC(T)}$ can be expressed as:

$$\sigma_{DC} = \frac{\sigma_0}{\sqrt{T}} \exp\left[-\frac{T}{T_0}\right]^{-1/4} \text{ ... } \mathbf{(5)}$$

where σ_0 and T_0 are parameters of Davis-Mott model. The Activation energy corresponding to first case suggest the existence of high density of localized states while the second case represents carrier transport across grain boundaries by thermal excitation. Fig.4 shows a fit behaviour represented by Eq. (5) which is reasonably good for temperature in the range 300 - 360 ^{0}K. Mott parameters σ_0 & T_0 were extracted from the best fit line and obtained value of σ_0($K^{1/2}$ S cm^{-1}) have changed from 3.03 $X10^7$ to 5.11 $X10^{16}$ and T_0(^{0}K) value have been changed in the range 2.99 $X10^7$ to 1.678 X 10^9 for uncapped and PVA-capped ZnS samples.

CONCLUSION

It is possible to produce ZnS nanoparticles using PVA as a capping agent in order to control the growth of particles using a simple chemical precipitation method. XRD results confirmed formation of wurtzite structure of ZnS nanoparticles. TEM image shows spherical shaped morphology. The optical band gap values of ZnS nanoparticles have changed from 3.8 to 4.5 eV with the doping of capping agent. Electrical conductivity behaviour of as synthesized samples has been well described by mott-davis model.

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ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

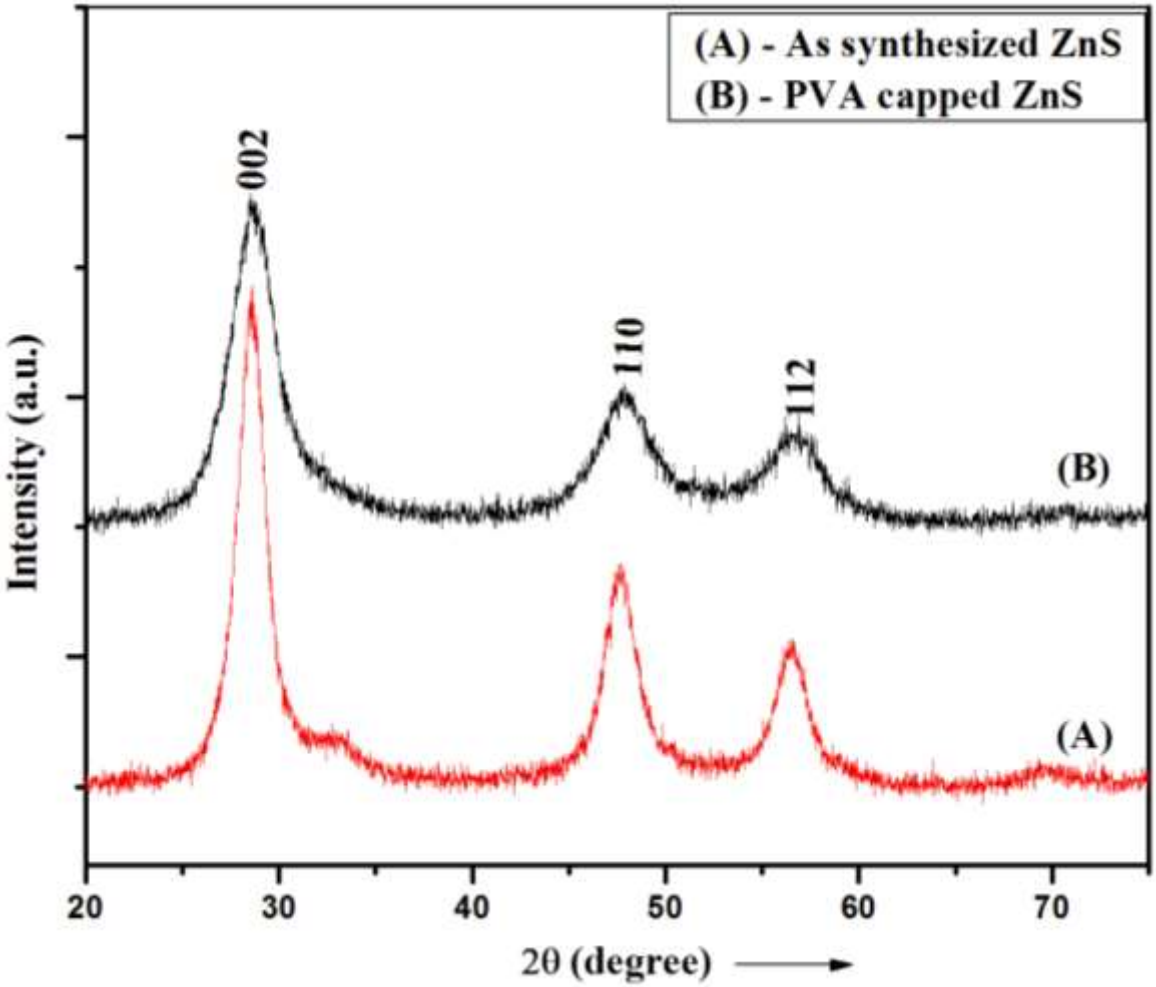

Fig. 1 XRD pattern of uncapped and PVA capped ZnS powder sample

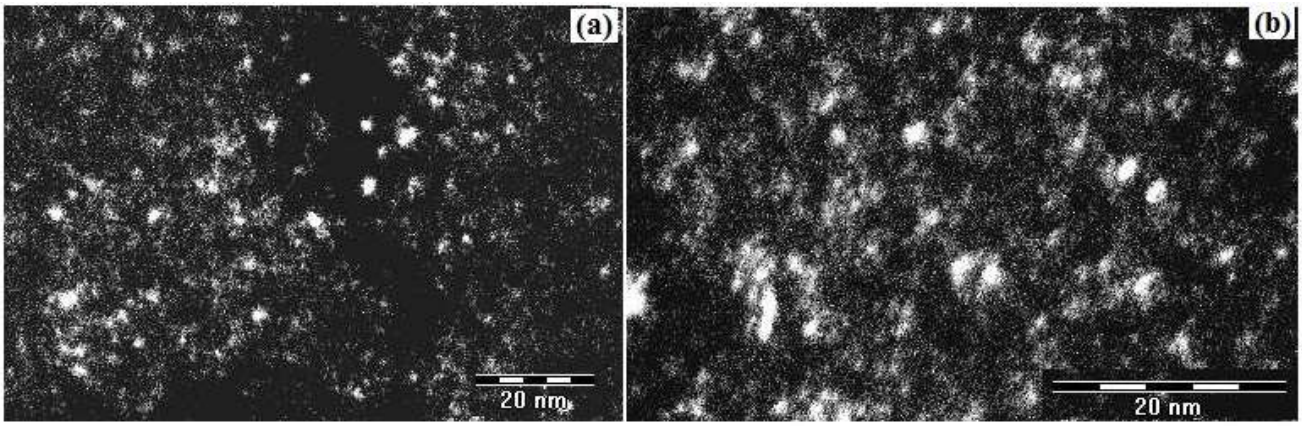

Fig. 2 TEM image as synthesized (a) and PVA-capped ZnS (b) nanoparticles

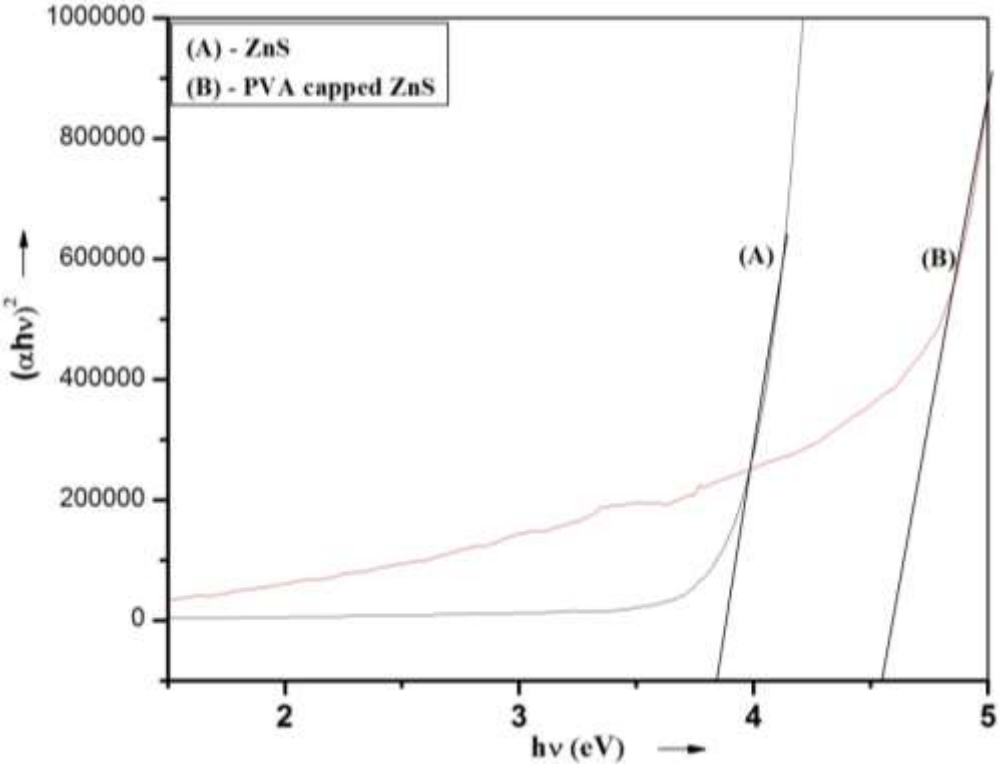

Fig 3 Optical band gap graph of as synthesized and PVA capped ZnS nanoparticles

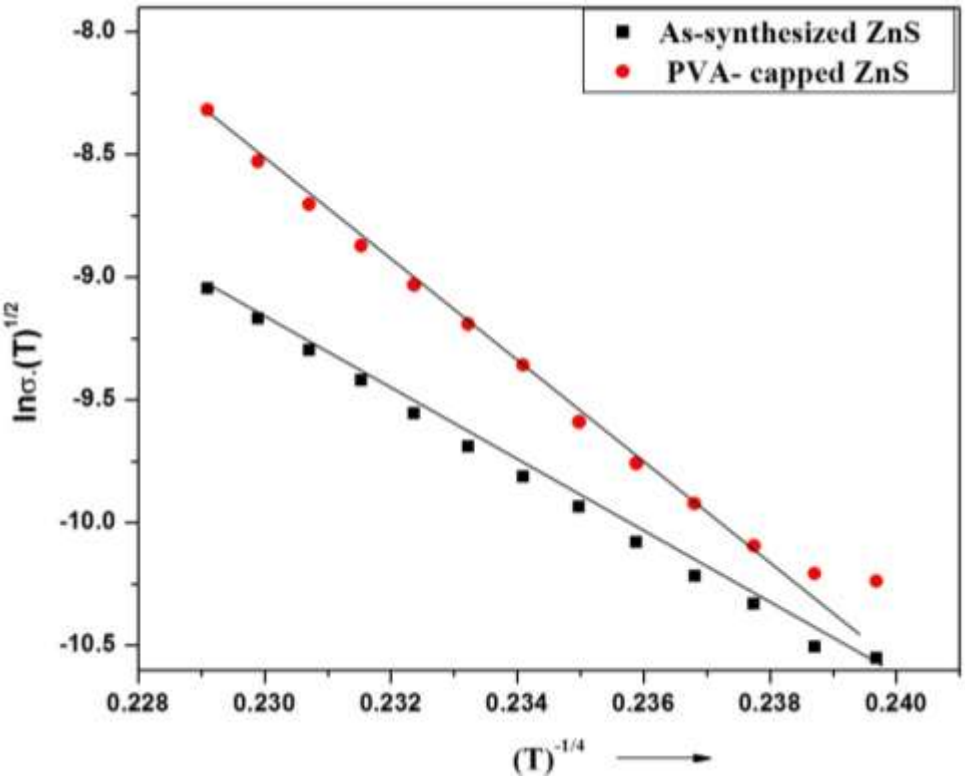

Fig. 4 Electrical conductivity graph of uncapped and PVA capped ZnS nanoparticles

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

Table.1: Particle size and optical band gap data for as synthesized and PVA-capped ZnS samples obtained from XRD, TEM and UV-Vis experiments

Particulars of ZnS Sample	Optical Band gap (eV)	Particle Size (UV-Vis analysis) nm	Crystallite Size (XRD analysis) nm	Particle Size (TEM analysis) nm
As-synthesized	3.84	3.22	4.7	~ 5
PVA-capped ZnS	4.55	1.65	2.7	~ 3