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Effect of Band Gap on optical properties of ZnS nanoparticles

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Abstract

In the current study, PMMA and CTAB were used as capping agents during the chemical co-precipitation process to create both uncapped and capped ZnS nanoparticles at ambient temperature. ZnS nanoparticles' structural characteristics were examined using an X-ray diffractometer (XRD), a transmission electron microscope (TEM), and an investigation of their optical characteristics utilizing UV-VIS absorption and photoluminescence studies. According to XRD examination, the samples were made up of cubic zinc blende particles that ranged in size from 3 nm to 5 nm. The Scherrer formula was used to determine the sample sizes. The production of ZnS nanoparticles with nearly uniform spherical shapes was discovered by TEM investigation. A noticeable blue shift may be seen in the UV-VIS absorption spectra. Analysis of photoluminescence revealed that as particle size is decreased, the emission peak shifts to the shorter wavelength side. Increased fluorescence intensities were seen in capped samples.

KeyWords: Co-precipitation method, II-VI group Semiconductor particles, Structural, optical and Photoluminescence properties.

1. Introduction

The great reliance on particle size has led to the emergence of the synthesis of nanomaterials as a significant research field in recent years. Since they are used in optoelectronic devices and have a wide range of bandgaps, II-VI class inorganic semiconductor materials including ZnS, CdS, CdSe, and ZnSe have demonstrated their versatility. Due to its use in cathode ray tubes, efficient phosphors, flat-panel displays, solar cells, etc., ZnS has gained a lot of interest. According to descriptions of semiconductor nanocrystals, there are two states of matter: individual molecules and bulk[1-8]. An increase in the dominance of surface atoms and the presentation of quantum mechanical features as a result of the transition from bulk to nanoparticles boosts a material's chemical reactivity. Chemical synthesis has the benefit of producing size-controlled, unaggregated nanoparticles. A benefit in creating new composite materials with optimum qualities for varied applications may come from the tunability of nanoparticle properties by altering their size. However, the limited scope of these materials' uses is caused by various non-radiative relaxation processes. Surface-related relaxation is a significant non radiative relaxation defects. These nanoparticles' crystallites are primarily responsible for the majority of their physical or chemical characteristics. As these crystallites aggregate to create primary particles, they continue to grow in size. If the growth of the particles is not controlled, they may aggregate and settle as a result of Vanderwaals interactions and Ostwald ripening. Organic stabilizers (polymers), such as sodium polyphosphate, Mercaptoethanol, PMMA, CTAB and Thiourea, can be added during the chemical synthesis for capping in order to restrict the formation of nanoparticles. Such materials are used in optical sensors, light emitters, phosphors, and luminescent devices. Such materials are used in optical sensors, light emitters, phosphors, luminescent devices, and other things[9–11]. Recently, fluorescent labeling by semiconductor nanoparticles for biological detection and applications in many domains is the outcome of the advancement of luminous nanoparticles by effective capping. The addition of organic chemicals will change the shape, size confinement, and luminescence behavior of inorganic semiconductors. Semiconducting nanoparticles have been created using a variety of scientific techniques, such as chemical co-precipitation, chemical vapour deposition, hydrothermal heating, and the sol-gel method, among others. In order to investigate several intriguing features, an attempt has been made in the current work to synthesis and characterize PMMA(Poly methyl methacrylate) and Cetyl trimethyl ammonium bromide (CTAB) capped ZnS nanoparticles by chemical coprecipitation technique.

2. Experimental technique

In the current investigation, ZnS quantum dots were made using the chemical co-precipitation approach both without and with capping agents. For the creation of nanoparticles, all of the chemicals were of AR grade and employed without additional purification. Zinc acetate, sodium sulfide, and the capping agents PMMA($C_5H_8O_2$) and Cetyl trimethylammoniumbromide (CTAB) ($C_{19}H_{42}NBr$) were the compounds utilized.

2.1 ZnS Without capping agents: 6.5847 grams of zinc acetate are dissolved in 150 ml of distilled water and methanol to create a 0.2 M solution. the 0.2M Na_2S solution 3.1216 grams were dissolved in 200 cc of distilled water and methanol to make the preparation. The 0.2M zinc acetate solution is mixed continuously with a magnetic stirrer for 3–4 hours as 0.2M sodium sulphide solution is added dropwise. After centrifugation, the white precipitate is collected and cleaned three to four times with distilled water and ethanol to get rid of contaminants.

2.2 ZnS With capping agents: In two separate beakers containing the 0.2M zinc acetate solution, 0.1M solutions of PMMA and CTAB were combined for 30 minutes with magnetic stirring. After that, each beaker receives dropwise additions of 0.2M Na_2S solution while being continuously stirred for 3 to 4 hours, or until precipitates develop. Following centrifugation, precipitates were recovered and cleaned three to four times with distilled water and ethanol. The precipitates were ground into a fine powder and dried under a 60 watt lamp for three hours.

3. Instruments

Using the PXRD Pan analytical X'PERT Pro MPD diffractometer and CuKα radiation (0.154 nm), the sizes of all the samples are calculated. At room temperature, XRD data is gathered over the 20°–80° range. The Scherrer formula is used to determine the particle size. TEM (Philips CM 200, Operating voltage 20-200 kV, Resolution- 0.24nm) analysis is used to study the structural characteristics of the materials. The samples' UV-Visible absorption spectra is examined between 200 and 600 nm. Using the WITEC -300 Raman PL Setup, photoluminescence characteristics are investigated between 300 and 900 nm.

4 Results and Discussion

4.1 XRD Studies:

Three diffraction peaks, which correspond to the (111), (221), and (311) planes of the cubic ZnS, were visible in the XRD pattern. Due to the size impact, the peaks were widened, which suggests the development of nanoparticles. The Debye-Scherrer formula is used to calculate the average particle size

$$D=K\lambda/\beta\cos\theta \qquad (1)$$

Where K is the scherrer constant, which is equal to 0.9, θ is the diffraction angle, D is the particle size, β is the full width at half maximum (FWHM) in radians, and λ is the wavelength of Cu-K radiation, which is equal to 0.154 nm[9].

Stokes-Wilson relation is also used to compute the average strain [11].

$$\text{Strain} = 4\,\beta\tan\theta \qquad (2)$$

The relation $d= \lambda/2\sin\theta$ is used to compute the interplanar spacing d. where θ is the diffraction angle and λ is the x-ray radiation wavelength. Equation 3, is used to obtain the lattice constant for each plane [11].

$$a=d(h^2+k^2+l^2)^{1/2} \qquad (3)$$

Table 1: Structural properties of ZnS (uncapped and capped) nanoparticles

Sample	2θ in deg	plane	Interplanar spacing d(nm)	Lattice constant a (nm)	D (Size) in nm	Strain
1. ZnS	28.77	(1 1 1)	0.3087			
	47.82	(2 2 0)	0.1895	0.5350	4.626	0.034
	56.85	(3 1 1)	0.1617			
2.ZnS +PMMA	28.67	(1 1 1)	0.3112			
	47.82	(2 2 0)	0.1895	0.5370	3.330	0.058
	56.85	(3 1 1)	0.1633			
3. ZnS+ CTAB	28.77	(1 1 1)	0.3089			
	47.72	(2 2 0)	0.1902	0.5354	4.006	0.0422
	56.43	(3 1 1)	0.1622			

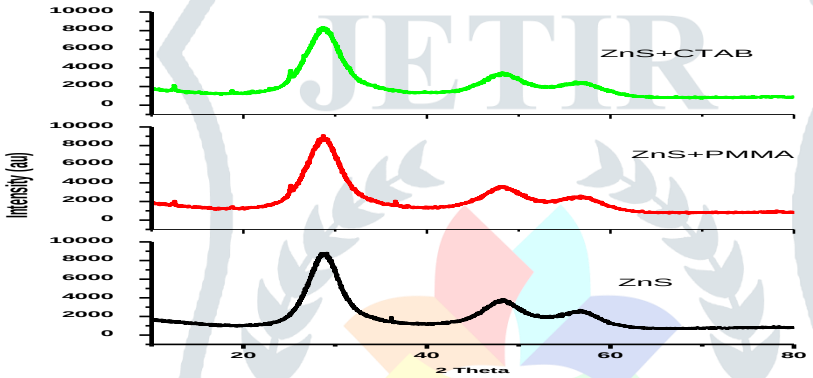

Fig 1: X-Ray Diffraction of pure ZnS and CTAB and PMMA capped ZnS nanoparticles

4.2 Studies on optical absorption

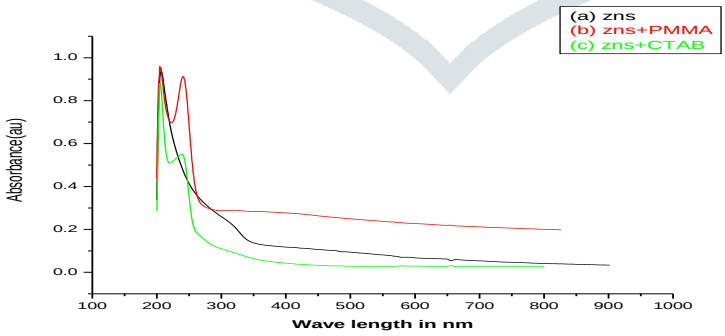

Fig 2: UV-Visible absorption of pure ZnS and CTAB and PMMA capped particles.

Figure 2 displays the absorption spectra of ZnS nanoparticles created using various capping agents. Peaks in the absorption were seen in the wavelength range of 200 nm to 250 nm. Two peaks were observed for capped samples due to different morpology.

When calculating band gap energy, use the formula $E_g=hc/\lambda$ (4)

where the plank's constant, the speed of light in a vacuum, the wavelength, and the band gap energy of nanoparticles are each represented by a letters h, c and λ respectively.

The decrease in size of the nanocrystals is connected to the blue shift of the absorption edges for distinct nanocrystals. nanoparticles' quantum confinement effect is responsible for this phenomenon [12].

Effective mass approximation, or EMA, is a theoretical concept put forth by Brus that connects a material's effective band gap with its particle size. The band gap for each particle is computed using the average crystallite size found in the X-ray diffraction spectrum. The results are shown in Table 2. The optical size of nanocrystallites is also determined using Brus equation [13] by applying confinement effects.

$$E_{g(nano)}=E_{g(bulk)}+h^2/8r^2(1/m_e+1/m_h)-1.8e^2/4\pi\varepsilon_o\varepsilon_r r \quad \ldots\ldots\ldots\ldots (5)$$

E_g(nano) in ev stands for the band gap energy of bulk ZnS, m_e and m_h stand for the electron and hole effective masses, r stands for the particle's radius in nm, ε_o stands for the permittivity of free space, and ε_r stands for the sample's permittivity. E_g = 3.68 eV, m_e = 0.34 m_o, and m_h = 0.23 m_o for bulk ZnS; m_o = free electron rest mass. The coulombic term, the last term in equation (5), is typically ignored. The size of nanoparticles was determined by replacing the band gap energy values of synthesized samples in equation (5), and the results are shown in Table2.

Table 2 : Band gap and size of ZnS (uncapped and capped) nanoparticles.

Sample	Absorption peak in nm	Band gap in (ev) from absorption spectra	Band gap (ev) from Brus eq	Crystal size in nm from EMA	XRD	TEM
1. ZnS	206.5	6.015	4.53	2.170	4.626	4.678
2. ZnS+ PMMA	204.5	6.074	5.76	2.140	3.330	3.362
3 ZnS+ CTAB.	206	6.030	4.90	2.162	4.006	4.058

These findings lead us to the conclusion that all samples exhibit a distinct blue shift in band gap with respect to bulk ZnS (band gap of bulk ZnS is 3.68 eV for cubic structure). This results from quantum confinement effects changing the valence band and conduction band [14]. When the particle size is smaller than the Bohr radius (roughly 2.5 nm), strong confinement is observed. As a result, the band gap can be determined from the maximum of the absorption peak when strong confinement causes absorption peaks to appear in the absorption spectra. Results for ZnS (with and without CTAB) were substantially identical.

Two exciton peaks at 204.5 nm and 238.19 nm were seen in the absorption spectrum of capped ZnS, indicating the creation of distinct morphologies due to carboxyl and halogen group of PMMA and CTAB. The results demonstrate that the Brus equation cannot be expected to be quantitatively accurate for very small particles because the band gap obtained from Brus equation was less than the band gap calculated from absorption peak for each particle.

4.3 TEM Studies

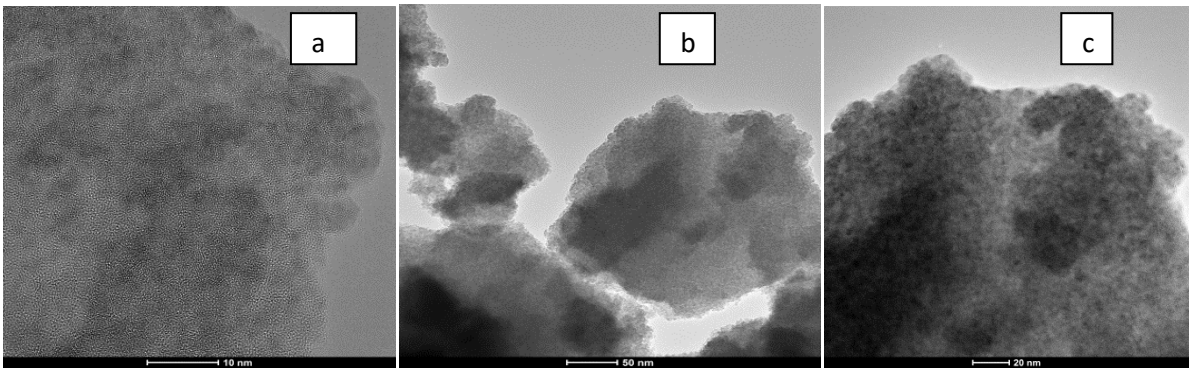

Fig 3: TEM images of (a)ZnS (b)ZnS+PMMA and(c)ZnS+CTAB Capped nanoparticles.

Figure 3 displays the TEM and images of uncapped ZnS, Thiophenol-capped ZnS, and CTAB-capped ZnS nanoparticles. Each image demonstrates that the predicted sizes were closely matched to the XRD measurements, and the particles are monodispersed and nearly spherical in shape. [15]

4.4 Studies on photoluminescence

Figure 4 displays the photoluminescence spectra of ZnS nanoparticles (both capped and uncapped) that were captured at a wavelength of 355 nm. Uncapped ZnS nanoparticles displayed a large emission peak at 439 nm, which was attributed to the host ZnS, as seen in photoluminescence spectra. This blue emission can be attributed to a self-activated center that likely developed between a Zn vacancy and a shallow donor linked to a Sulfur vacancy [16,17]. Peaks at 426 nm and 431 nm, respectively, were visible in the presence of PMMA and CTAB -capped particles. ZnS nanoparticles with capping agents have a relative higher emission intensity than ZnS without capping agents. This was anticipated since uncontrolled nucleation and development of particles occurred in the absence of a capping agent, leading to the defect states.

However, improved luminescence was seen in capped nanoparticles due to the capping agents' surface modification, which had the impact of decreasing surface defects, as well as the transfer of energy from chemisorbed capped molecules to interstitial sites and vacancy centers. The quantum size effect was used to explain how luminescence intensity increases as particle size decreases [18,19]. The valence band edge shifts southward as the particle size decreases. Because of this, the photon that is released has a somewhat larger energy, which causes photoluminescence to peak at a shorter wavelength [20]. PMMA capped ZnS nanoparticles displayed the highest luminescence intensity when compared to CTAB. This may be due to carboxyl group of PMMA. [21-25]

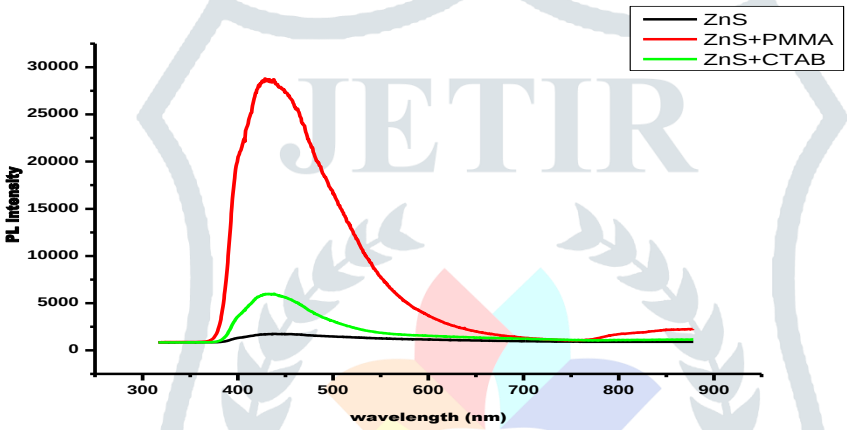

Fig 4. Photoluminescence spectra of Uncapped and Capped ZnS nanoparticles.

5 Conclusions

PMMA and CTAB were used as the capping agents in the co-precipitation process to create both uncapped and capped ZnS nanoparticles. The produced samples were examined using a variety of characterisation techniques, including XRD, TEM, UV-Visible absorption, and photoluminescence investigations. The cubic crystalline structure of ZnS is supported by XRD and TEM patterns. Sizes of nanoparticles determined using the Scherrer formula are closely matched to sizes calculated using TEM images. All the three samples show a blue shift in the peak of the UV-visible absorption spectra relative to the bulk. As the particle size is decreased, the peak of the photoluminescence spectrum likewise migrated to the shorter wavelength side. When compared to uncapped particles, capped particles displayed the highest PL intensity. ZnS nanoparticles coated with PMMA exhibited more intensity than those coated with CTAB, this might be because PMMA contains a carboxyl group.

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Conflicts of interest

The authors declare that they have no conflicts of interest

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