Crystal engineering of ZnS by cationic and anionic surfactant-cum-solvent

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Abstract
High temperature (1020 °C) wurtzite phase of ZnS is highly valuable multifunctional wide-band gap semiconductors. However it is difficult to stabilized wurtzite phase at room temperature. In the present study, the high temperature phase is successfully stabilized at low temperature (120 °C) in presence of cationic surfactant-cum-solvent like ethanolamine (ENA) and Oleylamine (OLA). While, the use of anionic surfactant likes ethylenediamine tetra acetic acid (EDTA) could not induce cubic to wurtzite phase transformation in ZnS. X-ray diffraction study confirms the cationic surfactant-mediated phase transformation of ZnS. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images shows nanoscale dimensions of as synthesized ZnS. The coupling between surfactant molecules with ZnS is confirmed by Fourier Transform Infrared spectroscopy. A significant reduction in the phase transition temperature of ZnS from 1020 to 120 °C is achieved as compared to the bulk transition temperature (1020 °C). The role of cationic and anionic surfactants-cum-solvent on mechanisms of phase transformations of ZnS is discussed.

1. Introduction

The intrinsic crystal structures of semiconductor have an important effect on its physical and chemical properties. The inherent properties of semiconductor can be tailored by controlling size, structure and morphology \([1–4]\). Semiconductors nanoparticles exhibit unique electronic and optical properties mainly originate from quantum confinement effect. The structure dependent physical properties such as mechanical, thermal, magnetic, etc are also valuable in the field of research \([1, 5, 6]\). Therefore, the investigation of parameters influenced on phase transformation is of great interest in condensed matter physics or material science \([2, 7]\). The experimental parameters such as, interfacial energies, surfactants, solvents, templates etc other than temperature and pressure have been found to influence on structural transformations due to aggregation, atomic motions and modifications in the kinetic energies at nanoscale \([2, 8–10]\).

Particles agglomeration is main concerned in nanoparticles synthesis. To avoid agglomeration, surfactant is more commonly used. In addition to that, surfactants have been reported in inducing phase transformation of many semiconductor nanoparticles. Even a small amount of surfactant can efficiently affect the nucleation and growth kinematics which in turn can induce crystal modification \([11, 12]\). In general, cationic and anionic surfactant used for the synthesis. Cationic surfactants are identified as positively charged hydrophilic head. This positive charge on head may be permanent or only exist in certain pH range. Mostly cationic surfactant corresponds to nitrogen compounds having fatty amine salts and quaternary ammoniums, with one or several long chain of alkyl type. Anionic surfactants are having negatively charged head group.

Among various II–VI group semiconductors, ZnS is wide band gap semiconductor ever discovered having tremendous importance in the field of research due to its outstanding applicability in several fields such as sensors, photocatalysis, imaging, solar cells, electro-optic devices, flat panel, H\(_2\) evolution etc \([13–19]\). Basically it is a trimorphic crystal with Zinc blende, rhombohedral and wurtzite as three polymorph of it. Rhombohedral structure is an intermediate phase between isometric zinc blend and directional wurtzite structure which forms...
at 600 °C. While among other two; sphalerite (cubic phase) is most stable at ambient condition with band gap of 3.66 eV in bulk. This phase has face centered cubic structure having dual structural motif, in which Zn occupies (0,0,0) and S occupies (¼, ¼, ¼) sites. And wurtzite (hexagonal) phase is thermodynamically metastable state with a band gap of 3.77 eV at room temperature. This structure is stable at 1020 °C but it melts at 1650 °C. In wurtzite structure Zn occupies (0,0,0) or (1/3, 2/3, 0) and S occupies (1/3, 2/3, 0) or (1/3, 2/3, 0.3748) sites. In both structures, Zn and S are tetrahedrally bonded with the only difference in the stacking sequence of atomic layers. In cubic Zn and S stacked in ABCABC…. pattern, while that in hexagonal structures in ABABAB…. pattern, while that in hexagonal structures in ABABAB…. pattern, while that in hexagonal structures in ABABAB…. pattern. These differences in their crystalline structure and size can lead to considerable changes in the effective masses of electrons, holes, and energy gaps. The properties of materials change dramatically with size, including thermodynamic stability. Zhang et al. in his experimental work and molecular dynamics (MD) simulations at 300 K in vacuum, have suggested that particles having wurtzite phase are more stable than that having cubic phase as we go to nanoscale regime of about 7 nm. A low-temperature preparation of hexagonal ZnS is desirable because the prepared wurtzite nanostructures can meet the thermal stability required for reliable optoelectronic device operation. Also it is more desirable structure for its optical properties than the cubic structure. But the major challenge is to stabilize high temperature wurtzite phase at low temperature. Organic molecules especially the surfactant can help in phase transformation from cubic to wurtzite by reducing the difference in free energy of formation between the two polymorphs. In earlier reports, the phase transformation from cubic to wurtzite in a low temperature synthesis under certain conditions has been reported. Yu Zou et al. have synthesized CdS nanoparticles for photovoltaic application in both the phases i.e. cubic and hexagonal at low temperature 280 °C using a cationic surfactant CTAC. Pai-Chia Kuo et al. prepared ZnS nanorods having wurtzite phase at low temperature of 200 °C in presence of ethylenediamine as surfactant or partial solvent by simple co-precipitation and hydrothermal method. Nisha et al. have synthesized Cds nanosheets in both the phases i.e. cubic and hexagonal at low temperature 120 °C in presence of CTAB as surfactant. Acharya et al. have reduced wurtzite-to-cubic phase transformation temperature of ZnS from 1020 °C to 170 °C by using Ethylenediamine (EDA) as surfactant. There are various reports on reduction of phase transition temperature ZnS by using surfactant or partial solvent with water. However, very few surfactants have been found to mediate phase transitions. Exact role of surfactant on the reduction of phase transition temperature is ambiguous and further study is needed to understand it more comprehensively.

In the present attempt, we use various cationic and anionic surfactant-cum-partial solvent with water like Ethylenediamine tetra acetie acid (EDTA), Ethanolamine (ENA), and Oleylamine (OLA) for synthesis of ZnS NPs. The role of content of surfactant in water on phase transformation of ZnS is closely monitored by using x-ray Diffraction. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) tools are used for microstructural analysis. Role of cationic and anionic surfactant-cum-solvent on phase transformation are comprehensively explained. Novel mechanism of surfactant induced phase transformation is proposed.

2. Experimental

2.1. Materials
All chemical reagents were procured from Merck and used as it is without further purification. Double distilled water, Ethylenediamine tetra acetie acid; Ethanolamine and Oleylamine were used to prepare the aqueous solutions. The salts of Zinc acetate [(Zn(CH3COO))2, 2H2O] 98%), was used as source of metal ions. The sodium sulfide flakes (Na2S.xH2O) was used as precipitation reagent of metal ions.

2.2. Synthesis of ZnS nanoparticles
0.1 mole of Zinc acetated was added in 100 ml of Surfactant; double distilled water mixture. Surfactant was taken x% (volume in ml) and H2O is taken (100-x)% (volume in ml) and x has the values 0, 20, 50, 90, 100. The mixture was kept for constant stirring on hot plate with magnetic stirrer for 30 min at 60 °C. Then 0.1 ml of Na2S was added to get white solution. The resultant solution was stirred for 30 min at 60 °C for homogeneous mixing. The solution was then transferred into a flask with refluxore and condenser and preceded at 120 °C for 24 h. The obtained solution was washed with double distilled water by centrifuging it for 15 min at 6000 rpm and precipitated is dried at 60 °C in hot air vacuum oven.

2.3. Characterizations
The structure and phase purity of the sample was checked by x-ray powder diffraction (XRD) using PAN analytical X Pert Pro x-ray diffractometer equipped with copper target (λCuKα1 = 1.5405 Å). The data were collected with a step size of 0.016 711° and step time of 3.08 s. The Rietveld refinement of the XRD pattern was...
done by Full Prof Suit. Scanning electron microscopy (SEM) images were obtained on JSM-7600F, equipped with an energy dispersive x-ray spectroscopy. Energy dispersive x-ray spectroscopy (EDX) was done to confirm chemical purity and stereochemistry of the sample. Transmission electron microscopy (TEM) images were obtained on a Philips CM200 transmission electron microscope with an operating voltage of 20–200 kV and resolution 2.4 Å. Absorption spectra were obtained on a Perkin Elmer Lambda 35 Serial No. 502512621910 UV-Vis spectrometer.

3. Result and discussion

3.1. Structural Transformation

Figure 1. shows the XRD patterns of EDTA mediated ZnS NPs. All XRD patterns are indexed by JCPDS file 800020 and well matched with zinc blend structure of ZnS. It could be clearly illustrated from the figures 1(a)–(d) representing the stabilized Cubic phase even for 100% of EDTA. However, broad nature of XRD peaks for all concentration of EDTA are evidence for fine size particles distribution of ZnS. Figure 2. shows the XRD patterns of Ethanolamine (ENA)-assisted synthesized ZnS. For the sample without ENA and 20% ENA, the diffraction peaks are observed at 28.85°, 48.01°, and 56.99°. These peaks are identified due to (111), (220), and (311) planes of cubic or zinc blende structures of ZnS (JCPDS no 800020). The effect of ENA on the phase transformation of ZnS is clearly evident from figure 2. With an addition of ENA = 50% into an aqueous
solution, the XRD pattern shows the emergence of new additional peaks. For 50% EN, four new peaks are emerging at $2\theta = 27.49^\circ$, $31.09^\circ$, $40.28^\circ$, and $52.61^\circ$ with three old peaks overlapping at $28.87^\circ$, $48.04^\circ$, and $56.74^\circ$. All the peaks are recognized with planes (100), (002), (101), (102), (110), (103), and (112) of the wurtzite phase of ZnS (JCPDS card no. 751534). All diffraction peaks of the sample are matched well with that of the wurtzite phase of ZnS crystal, indicating that the wurtzite phase has been formed in the sample in the presence of ENA. With increasing ENA concentration, the relative intensity ($I_{(hkl)}/I_{(002)}$) of the new peaks due to (100), (101), (102), and (103) planes is found to be systematically increasing (see figure 3). The total scattering from each plane depends directly on the distribution of atoms in the structure. This is ultimately related to or measures the peak intensity of the respective plane, and thus reflects the degree of crystallinity of that plane. With increasing percentage of ENA in the reaction solution, an increasing trend of relative intensity is observed indicating that the degree of crystallinity of the hexagonal or wurtzite phase of the ZnS is increasing with increasing ENA percentage. The crystallinity is also related to the concentration, reaction temperature, time, and the particle size measured. In the present work, there is high uniformity maintained in reaction conditions, while synthesizing all the samples, except a variation of ENA concentration in water. It implies that the variation in the degree of crystallinity observed here is only due to the different percentage of ENA used for sample preparation. This results with ENA as surfactant is analogous with our previous study with Ethylene diamine (EDA) as surfactant [2]. But, with ENA as surfactant, although the emergence of wurtzite peaks starts for little higher concentration i.e. at 50% of ENA, the degree of crystallinity achieved with ENA is higher (for low reaction temperature $120^\circ C$ and with only one primary amine) than that reported with EDA [2].

Figure 4 displays the XRD pattern of OLA mediated ZnS NPs. All the peaks are recognized with planes (002), (101), (102), (110), (103), and (112) of the wurtzite phase of ZnS (JCPDS card no. 751534). But in case of OLA as surfactant, the XRD data is little bit noise indicates low of degree of crystallite. The probable reasons for requirement of high content of OLA to induce phase transformation of ZnS can be associated with its chemical structure. It has long tail of fatty amine contained in the chemical structure leads to reduce solubility of the precursors in the solvent; which influences on reaction kinetics and thus nucleation growth [25]. The reaction kinetics is slowed down in presence of OLA. Thus high content of OLA is required to modify stacking sequence at nucleation stage, which is responsible for cubic-to-wurtzite phase transformation. Thus the degree of crystallinity of wurtzite phase of ZnS in presence of OLA is lower as comparative to other cationic agent. Like head tail of the surfactant also plays a very important role on the size, morphology and crystallinity of particles [26–28]. OLA has higher boiling point of about $350^\circ C$ [26] which is far greater than the reaction temperature in our work. Thus long tail surfactant takes higher temperature and time to get inside the lattice structure to produce phase transformation. Table 1. depicts the detailed information of the surfactant used.

To get more insight of structural information, Rietveld refined of XRD pattern of ZnS samples synthesized with ENA as surfactant and solvents are shown in figure 5. All these samples yield satisfactory fit by Rietveld refinement having $\chi^2$ in the range of 1–2 except for 20% ENA content. For 20% ENA, the data is found unable to fit properly by Rietveld refinement. The samples exhibit mixed phases i.e. Cubic Zinc Blende Structure for ZnS with a space group of F-43m and Wurtzite confirmed with a space group of P 63 mc. The parameters obtained from Rietveld Refinement are tabulated in table 2.

The variation of lattice parameters $a^*$, $b^*$, and $c^*$ as a function ENA content (see figure 6) demonstrate surfactant-induced phase transformation process of ZnS. A abrupt change in the lattice parameter of cubic...
phase can be clearly observed after ENA percentage of 50%, which is the phase transformation percentage and have wurtzite to Cubic ratio approximately equal to 1:1. Similar to this lattice parameter c of wurtzite phase also shows decreasing trend upto 50% and thereafter it increases and stays relatively constant for further addition of ENA. While the lattice parameter a = b of wurtzite phase shows reverse trend, in which a continuous increase in lattice parameter is observed with the increasing percentage of ENA.

To analyze more comprehensively the surfactant-cum-solvent mediated phase transformation, three dimensional view of crystal structure of ZnS are generated by the VESTA program by using XRD data. The parameters namely, bond angle, bond length difference, and tilting angle are extracted out from the fitting. The accuracy of extracted data from VESTA is limited, but trend of variations of parameters are obtained from the analysis. The pictorial representation of the as-obtained crystal structure of ZnS for different ENA content as

**Table 1. Detailed information of surfactant used.**

| Name and Chemical formula | Chemical structure | Molar Mass (g/mol) | Solubility in water | Density (g cm⁻³) |
|---------------------------|--------------------|-------------------|---------------------|-----------------|
| Ethanolamine (ENA) [C₂H₇NO] | ![Ethanolamine](image) | 61.08 | Miscible | 1.01 |
| Ethylenediamine (EDA) [C₂H₄N₂] | ![Ethylenediamine](image) | 60.1 | Miscible | 0.9 ± 0.1 |
| Oleylamine (OLA) [C₁₈H₃₅NH₂] | ![Oleylamine](image) | 267.49 | Insoluble | 0.823 |
| Ethylenediamine tetra acetic acid (EDTA) [C₁₀H₁₆N₂O₈] | ![Ethylenediamine tetra acetic acid](image) | 296.27 | Miscible | 0.86 |

**Figure 4.** XRD pattern of ZnS in presence of OLA (100%) as surfactant.

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solvent during synthesis are depicted in figures 7(a) and (b), respectively. In both the cases, Zn occupies the central position with four equally spaced S atoms forming a tetrahedral geometry. In cubic structure all bond lengths are same but different for the materials having different percentage of ENA. While the bond angle and bridging angle are same (109.47°) in structure as well as in all ZnS samples. In case of Wurtzite structure bond length and bond angle are quite different in different direction. Letters ‘1, 2, 3 and 4’ are used to designated bond length along four different direction of tetrahedral ZnS4. Bond length ‘2’ is quite large compared to the other

Table 2. Parameters obtained from Reitveld Refinement.

| % of ENA in solvent | 20% | 30% | 50% | 70% | 90% | 100% |
|---------------------|-----|-----|-----|-----|-----|------|
| Goodness of fit (χ²) | 2.86 | 1.57 | 1.55 | 1.55 | 1.57 | 1.63 |
| % of phases present | Cubic | 99.97% | 99.97% | 49.40% | 4.21% | 2.09% | 0.46% |
| | Wurtzite | 0.03% | 0.03% | 50.60% | 95.79% | 97.92% | 99.54% |
| Lattice parameter | Cubic | 5.361 | 5.365 | 5.30 | 8.86 | 8.92 | 8.89 |
| | Wurtzite | 3.555, 3.73, 3.74, 3.80, 3.83, 3.81, 7.569 | 6.25 | 6.01 | 6.29 | 6.27 | 6.27 |
| Rp | 20.8 | 30.6 | 54.5 | 13.5 | 11.9 | 11.8 |
| Rwp | 20.5 | 26 | 48.7 | 16.5 | 14.8 | 14.6 |
| Rexp | 7.16 | 13.76 | 31.38 | 10.62 | 9.43 | 8.97 |

Figure 5. Reitveld Refinement of XRD pattern of ZnS samples having ENA as surfactant and solvent in (a) 100%, (b) 90%, (c) 70%, (d) 50%, (e) 30% and (f) 20%.

Table 2. Parameters obtained from Reitveld Refinement.
three bond lengths. The bond angle ‘1’ and ‘2’ are found same and bond angle ‘3’ and ‘4’ are same. The obtained data of bond angle and length from VESTA programme fitting are tabulated in table 3.

For more clarity of explanation, the plot on variation of bond length as a function of ENA content is elaborated as display in figure 8. Anomalous changes in bond lengths are observed around 50% ENA content, where the phase transformation is supposed to be started. The sudden rise in bond length of Cubic phase and bond length ‘2’ of Wurtzite phase are evidence for this phase transformation. The trend of Bond length versus percentage of ENA is closely matched with Lattice parameter variation. Similar to bond length, bond angles is also anomalously varying at around 50% ENA content (figure 9). The bond angles ‘1’ and ‘2’ increases upto 50% ENA and then suddenly drops at 70% and again increases thereafter. Exactly opposite trend is observed for other two bond angles. The trends of variation of lattice parameter, bond length and bond angles indicates ENA as a solvent is responsible to modify atomic arrangement at the time of nucleation and crystal growth during initial stages of synthesis reaction.

![Figure 6. Percentage of ENA versus Lattice Parameter.](image)

![Figure 7. Crystal structure of Wurtzite ZnS synthesized via conventional coprecipitation methods.](image)

Table 3. Bond lengths and Bond angles obtained from crystal structure.

| % of ENA in solvent | 20% | 30% | 50% | 70% | 90% | 100% |
|---------------------|-----|-----|-----|-----|-----|-----|
| Cubic Bond length A  | 2.321 | 2.323 | 2.295 | 3.837 | 3.861 | 3.852 |
| Wurtzite Bond length A | 2.837 | 2.342 | 2.13 | 2.535 | 2.476 | 2.404 |
| Bond Angle 1,2       | 104.79° | 109.98° | 112.1° | 105.47° | 106.65° | 108.42° |
| Bond Angle 3,4       | 103.67° | 108.96° | 106.7° | 113.16° | 112.14° | 110.5° |
| Bridging Angle 5      | 114.79° | 109.98° | 112.1° | 105.47° | 106.65° | 108.42° |
The first-hand information can be collected from this analysis that as phase transformation from cubic to wurtzite is only obtained in presence of cationic surfactant. The roles of cationic and anionic surfactant on phase transformation are needed to be investigated.

### 3.2. Surfactant induced phase transformation mechanism in ZnS

The two phases of ZnS viz. zinc blende and wurtzite differ in their stacking structures. The stacking sequence of the close-packed planes of zinc blend structure [the (111) planes] is represented by the ABCABCABCABC repeating pattern. While that of wurtzite structure [(001) equivalently to (002) plane] stacks by ABABABABAB repeating pattern [23]. In such a case, the stacking or twinning fault may develop during formation or growth of the nuclei initiate phase transformation [24]. Also the surface energy is different for different phases. The cubic phase have average surface energy of $0.86 \text{ Jm}^{-2}$ while wurtzite phase have average surface energy of $0.57 \text{ Jm}^{-2}$ [29, 30]. Basically the phase transformation caused by stacking or twinning fault, which is initiated by the change in surface energy of ZnS, takes place due to coordination bond between Zn$^{2+}$ (surface zinc atom) of ZnS and organic molecule [31].

The organic molecule used as surfactant-cum-solvent during synthesis mediate surface modification during nucleation the present study induced twinning and stacking fault is solely responsible for the phase transformation.

To understand the role of cationic and anionic surfactant-cum-solvent on the nucleation and growth process of ZnS during synthesis, in situ pH variation of the reactant is closely monitored. It is found that reaction proceed with cationic surfactant has alkaline nature, while the reaction carried out in presence of anionic surfactant has acidic nature. Reaction without surfactant is also acidic.

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**Figure 8.** Percentage of ENA versus bond length.

**Figure 9.** Percentage of ENA versus bond Angle.
Alkaline nature of reaction leads to negatively charged layers surrounding ZnS nuclei and thus adsorbs cationic species \([32]\). The cationic surfactant (ENA, OLA) molecule is active as a ligand, and lone pairs of electrons associated with nitrogen atoms interact with cationic zinc ions. The coordination bonding between ZnS and surfactant reduced the surface energy. The reduction in the surface free energy is mainly governed by the lattice plane distortion which induced twinning and stacking fault \([31]\). The process still continues to develop a stable phase of ZnS. It leads to zinc blend-wurtzite phase transformation. The process is schematically represented as \([2]\), at low percentage of cationic surfactant, it behaves only as capping agent to interact with the ZnS nanoparticles and thus can absorb on the surface of ZnS (see figure 10 ©). Thus the further growth of the particles inhibited, limiting the particle size to nanoscale regime. In this situation Zn\(^{2+}\) ions are not effectively chelated by surfactant, but the nucleation and growth of ZnS is chiefly administrated only by surface and volume free energies \([33]\). With increasing percentage of surfactant, Zn\(^{2+}\) ions are more effectively enfolded by amine (–NH\(_2\)) group of surfactant. In this situation, the lone pairs of electrons associated with nitrogen atoms interact with cationic zinc ions (see figure 10(d)) also the surface energy of the system changes. Under this circumstances, a complex layer of intermediate structure of ZnS(ENA) is formed, which leads to stacking faults, in presence of the S\(^{2-}\) ions (see figure 10(e)). The process still continues to develop a stable Wurtzite phase of ZnS (see figure 10(f)). EDA, ENA and OLA all are primary alkyl-amines, which acts as electron donor at elevated temperature and shows affinity to metals through their NH\(_2\) functional group \([31]\). EDA having two primary amine groups and high synthesis temperature can promote faster stacking fault in ZnS tending to faster phase transformation than ENA and OLA. But the degree of crystallinity achieved by ENA in this report is larger than that reported with EDA.

While in case of acidic medium, the ZnS nuclei surface is positively charged and thus attracts anionic surfactant having negatively charged head group (see figure 11(b)). In case of EDTA, there is negatively charged head group associated with acetic group, which cannot bind with zinc ion in ZnS.

Figure 10. Phase transformation mechanism in the presence of cationic surfactant. The (a) Cubic structure without surfactant, (b) cationic surfactant molecule, (c) adsorption of cationic surfactant on the negatively charged surface of ZnS, (d) (ZnS). Surfactant complex, (e) ZnS phase with stacking and twinning fault due to release of cationic surfactant, and (f) Hexagonal phase.
3.3. Microstructure by SEM and TEM

Figure 12 depicts the SEM image of as-synthesized ZnS nanoparticles having wurtzite structure along with EDAX in inset of the figure. Spherical morphology of as-synthesized ZnS could be clearly seen in cubic as well as wurtzite phases. Slight increase in particle size could be observed in wurtzite phase as compared to cubic ZnS, which have particles sizes in range of 7–14 nm. The particle size for wurtzite ZnS are found to be varying in between 25–32 nm. The rise in particle size can be assigned to surface coating layer on the particles surface.

Figure 13 depicts the TEM image of as-synthesized Cubic and wurtzite ZnS nanoparticles. Nanoscale dimensions of as-synthesized ZnS in cubic as well as wurtzite phases are clearly depicted from TEM images. But heavy agglomeration is detected in surfactant capped ZnS particles. SAED pattern in inset of the figure depicts concentric circles indicating the polycrystalline nature of ENA capped ZnS nanoparticles.

3.4. Optical studies

UV–vis Spectrum of ZnS with increasing percentage of ENA is shown in figure 14. The spectrum show clear anomaly in absorption edge around 315 nm. More precisely absorption anomaly are detected at 330 nm, 320 nm, 316 nm, 314 nm, 311 nm and 311 nm for ENA percentage of 0%, 20%, 50%, 70%, 90% and 100% respectively. There is about 10 nm, 20 nm, 14 nm, 16 nm, 19 nm and 19 nm of blue shift from the bulk counterparts ($E_g = 3.66$ eV for cubic and 3.77 eV of wurtzite). This may contribute to the quantum confinement.

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Figure 11. Phase transformation mechanism in the presence of anionic surfactant. The (a) Cubic structure without surfactant, (b) anionic surfactant molecule, (c) adsorption of anionic surfactant on the negatively charged surface of ZnS.

Figure 12. SEM image of (a) Cubic and (b) Wurtzite ZnS.
The optical band gaps ($E_g$) is found to be $3.75\,\text{eV}$, $3.885\,\text{eV}$, $3.934\,\text{eV}$, $3.959\,\text{eV}$, $4.01\,\text{eV}$ and $3.997\,\text{eV}$ for ZnS with ENA percentage of 0%, 20%, 50%, 70%, 90% and 100% respectively. The particle size at these wavelengths is calculated by the formula derived using the effective mass approximation model of Brus.

### 3.5. Fourier transforms study of ZnS

To further investigate the interaction between ZnS and surfactant, FTIR spectra were measured. The FTIR spectra of the as-synthesized ZnS with a different percentage of ENA are shown in Figure 15. The peak at 667 cm$^{-1}$ is assigned to the stretching band of Zn-S [34, 36]. Peak at 803 cm$^{-1}$ is assigned to the resonance interaction between vibrational modes of sulphide ions in the crystal, while the broad transmission peaks at 900–1560 cm$^{-1}$ are due to the oxygen stretching and bending frequency. 2352 cm$^{-1}$ in ZnS is due to the O-H stretching. The broad peak at 3375 cm$^{-1}$ corresponds to the O–H stretching vibration mode of water, indicating
the presence of moisture on the surface of ZnS. The FTIR spectra of ZnS with 70% and 100% of ENA clearly exhibit the presence of peaks related to ENA and ZnS. Increase in the intensity of peaks related to ENA, indicating the coupling between ENA molecules with ZnS. The peak at 867 cm\(^{-1}\) corresponds to C-H bending vibration; 1020 cm\(^{-1}\) and 1075 cm\(^{-1}\) are assigned due to C-O stretching modes, 1134 cm\(^{-1}\) are due to CH\(_2\) twist band. Also the peak at 2080 cm\(^{-1}\) and 2221 cm\(^{-1}\) are observed due to rocking mode of NH\(_2\) which is slightly shifted compared to reference. Also the peaks at 2882 cm\(^{-1}\), 2949 cm\(^{-1}\) and 3133 cm\(^{-1}\) can be related to the C-H stretching mode\([35, 37]\). Increase in the intensity of the ENA related peaks can be clearly detectable with an increase in percentage of ENA.

In conclusion, the phase transformation of ZnS from cubic-to-wurtzite, in the presence of ENA has been demonstrated experimentally. FTIR analysis ensures the presence of ENA at the surface of the wurtzite phase. The coupling between ENA molecules with ZnS has been confirmed by FTIR. The SEM and TEM study confirm the nanoscale morphology of ZnS. To investigate the suitability of other surfactant on phase transformation of ZnS, cationic and anionic both types of surfactant such as ethylenediamine tetra acetic acid (EDTA), Olylamine (OLA) and Ethanolamine (ENA) were used in the synthesis approach of surfactant-assisted synthesis of ZnS.

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