



# Simple, inexpensive way of fabricating high quality Zn(O)S nanoparticles by varying pH

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## ABSTRACT

In this work, a simple, inexpensive room temperature chemical bath deposition is proposed to synthesize high-quality Zn(O)S nanoparticles of varied composition. The band gap of these nanoparticles is found to alter by varying their chemical composition. Through this study, the formation of quantum confined ZnS and ZnOS nanoparticles as a function of pH is confirmed. A possible mechanism for the formation of these nanoparticles with respect to pH is discussed here.

## 1. Introduction

The drive to lower the cost of the solar cells and use of environment friendly materials, has led significant research in the pursuit of new low cost materials by using cost-effective fabrication techniques. To this end, Zn(O)S has attracted considerable attention among researchers, because of its higher stability, tunable band gap, non-toxicity and higher transparency. Infact  $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$  (CIGS) thin film solar cell with ZnOS buffer layer has yielded an efficiency of 22.3%, which is at par to this cell when used with the toxic CdS buffer layer (i.e., 22.6%) [1,2]. The ZnOS used in this CIGS solar cell was fabricated by using chemical bath deposition (CBD) technique, where the precursors were initially mixed and then pre-heated to 55 °C before deposition. Moreover, in literature, Zn(O)S films were fabricated by using a wide range of fabrication techniques [3–5]. Among these, CBD is an attractive technique because of its simplicity, low cost and also easy tunability in chemical composition. Often in CBD, nanoparticles are first synthesized, followed by their dispersion and/or dissolution in appropriate solvent, which then either spin / dip-coated or drop casted to make a thin layer on the desired substrate. Understanding the microstructure and overall properties of these nanoparticles is essential as these would then govern the overall behaviour of the films.

Hence, in this study, a simple, inexpensive, room temperature, CBD route was devised to prepare Zn(O)S nanoparticles with tunable chemical composition and optical band gap. To this end, non-toxic precursors were used and pH of these solutions was varied from 6.0 to 11.0. Then a wide range of experimental techniques were used to understand the overall microstructure and optical properties of these nanoparticles. The present work is essential as this is a simple, room temperature

technique and till date no single room temperature technique for synthesizing Zn(O)S could be found in the literature. To the best of our knowledge, Zn(O)S nanoparticle synthesis using wet chemical route have so far been reported only by Pandey et al. [6], where a higher temperature solvothermal method was used. Further, Zn(O)S has also been synthesized in literature using biological agents, like *E. Coli* by Wu et al. [7], through *Aegle marmelos* fruit extract by Pavan Kumar et al. [8] and recently through dye degradation by Chu et al. [9]. All these processes are complex in nature regarding their synthesis and involve multi-step processing and therefore time-consuming [10]. Designing low temperature (preferably room temperature) synthesis techniques for buffer layer deposition is extremely necessary as this process step is usually carried out after the fabrication of the other layers, like, absorber layer, contact, etc. in the thin film solar cell. Note that, a higher temperature synthesis of this buffer layer implied heating up of the entire heterostructure to the desired temperature, which would then lead to the interdiffusion of the chemical species present in the adjacent layers, hence altering these individual layer properties and thereby the overall device efficiency.

## 2. Experimental details

### 2.1. Sample preparation

In a typical experiment, fresh and independently prepared aqueous solutions of 0.2 M zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ; Zn precursor, 99.99% extra pure, Merck) and 0.3 M thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ; sulphur precursor, 99.99% pure, Loba Chemie) were mixed in the chemical bath and required amount of acid (HCl) or alkali ( $\text{NH}_3$ )

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was added to maintain the pH, varying in the range of 6.0–11.0. The reaction time was 1 h at room temperature, which was kept constant for all these experiments. The Zn(O)S precipitates were then collected and filtered with the help of vacuum filtration unit using 0.22  $\mu\text{m}$  millipore filter paper. Next, these nanoparticles were washed two times with ethanol and four times with milli-Q water. After washing, these samples were subjected to atmospheric drying (inside desiccator). The dried nanoparticles were then ground in mortar for further characterization.

In this work zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was used as zinc precursor as it is organic in nature. Earlier studies have suggested the suitability of an organic precursor over the inorganic ones like, zinc nitrate dihydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ), zinc chloride dihydrate ( $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in ZnS nanoparticle synthesis, as an organic precursor not only offers electrons to the unoccupied *d* orbitals of the metallic ion to form a coordinate covalent bond, but also can accept free electrons from the metal ion by using its antibond orbital to form feedback bonds [11]. This could then lead to faster reaction kinetics with  $\text{C}_2\text{H}_5\text{NS}$ , which is the rate limiting step for nanoparticle synthesis [12,13].

## 2.2. Microstructural and optical characterizations

A detailed microstructural characterization of these synthesized Zn(O)S nanoparticles were carried out by using combination of experimental techniques, like, Powder X-ray Diffractometer (PXRD; Model: D8 Discover, Supplier: Bruker Corporation), high resolution Transmission Electron Microscope (with Scanning Transmission Electron Microscopy (STEM) attachment) (HRTEM; Model: JEM 2100F, Supplier: Jeol) and Field Emission Scanning Electron Microscopy (FESEM; Model: JSM 7600F, Supplier: JEOL Ltd.) with Energy Dispersive Spectroscopy (EDS) attachment. The PXRD measurements were carried out in the  $2\theta$  range of  $20\text{--}90^\circ$  (step size of  $0.2^\circ$ ) with  $\text{Cu K}\alpha$  ( $\lambda = 0.15418 \text{ nm}$ ) radiation and was used to know the phase, crystallite size, micro strain and dislocation density of these particles. Further, HRTEM was used to give information about the phase and lattice parameter of these nanoparticles. For FESEM analysis, the Zn(O)S nanoparticles were first Pt coated before introducing into the FESEM chamber and then their overall morphology was determined using an accelerating voltage of 5–10 kV. The qualitative elemental analysis using STEM EDS attached with FEGTEM and EDS attached with FESEM were carried out by dispersing the powder sample in water following by drop casting on a carbon tape.

Optical properties (absorbance and optical band gap) of these synthesized nanoparticles were investigated by using UV–Vis spectrophotometer (Model: Specord @ 210 plus analytic, Supplier: Jena, Germany) in the wavelength range of 200–800 nm. Base line correction was performed with milli-Q ultra-pure water in silica quartz of 10 mm. To understand the defect states of these nanoparticles, Photoluminescence (PL) measurements (Model: Fluorolog, Supplier: Horiba) were carried out using 310 nm as excitation wavelength.

## 3. Results and discussion

Irrespective of pH, all these synthesized Zn(O)S nanoparticles were found to have grown in sphalerite crystal structure, with strong (111) orientation (see Fig. 1). Overall these particles were found to be spherical in shape (see Fig. 2(a–j)). The average crystallite size (*D*) of these nanoparticles were determined using the following equation [14–17]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where,  $\lambda$  is the wavelength of the X-ray radiation (0.15418 nm),  $\theta$  is the Bragg angle,  $\beta$  is the full width at half maximum (FWHM) of the (111) peak of the Zn(O)S nanoparticles.

*D* of these synthesized nanoparticles was found to vary in the range of 18.7–29.7 Å, suggesting the growth of smaller crystallites in these nanoparticles (see Table 1). Qualitative elemental analysis by EDS confirmed the formation of Zn(O)S, with cation-to-anion (i.e., Zn-to-(S

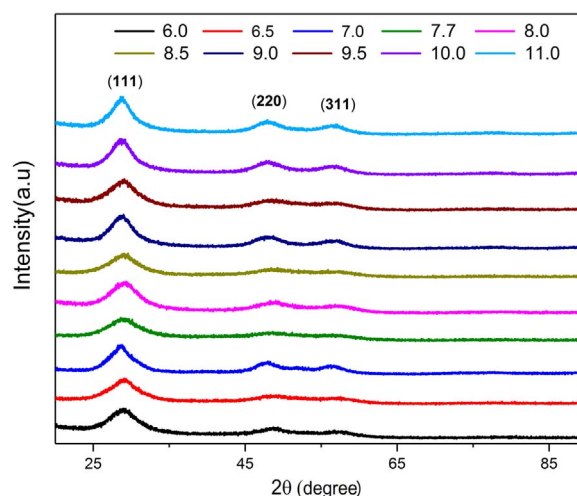


Fig. 1. Powder X-ray diffraction pattern of Zn(O)S nanoparticles synthesized by varying pH from 6.0 to 11.0.

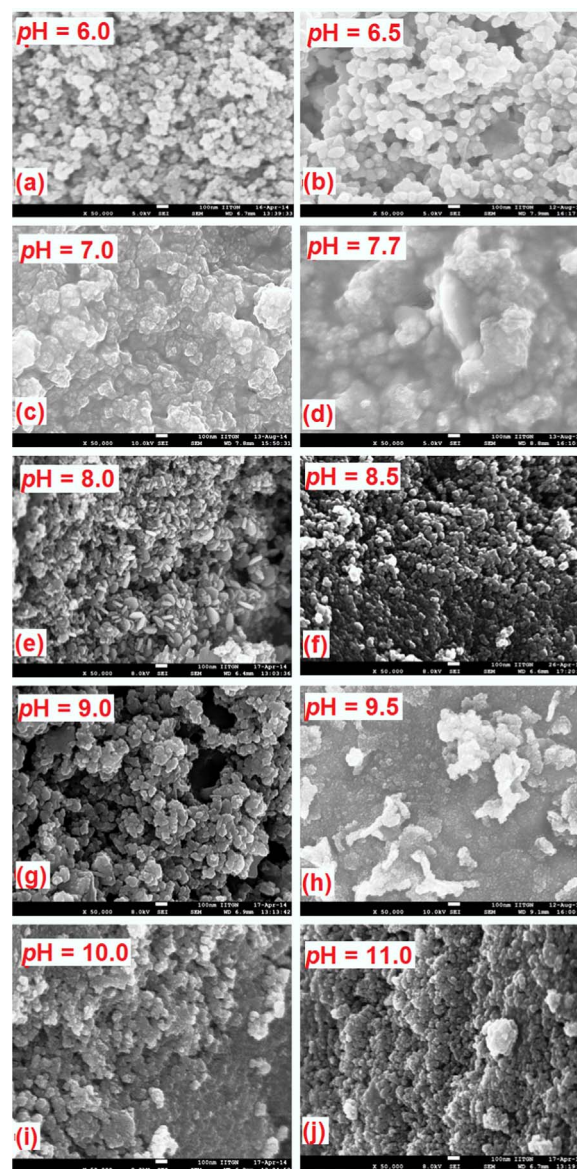


Fig. 2. (a–j) FESEM micrographs of Zn(O)S nanoparticles synthesized by varying pH from 6.0 to 11.0.

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