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Optimization of Thiourea as a Sulfur Source in the Synthesis of PBS Nanoparticles Characterization and Application

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Sulfur source concentration allows the properties of lead sulfide (PbS) nanoparticles used in optoelectronics, photovoltaics and catalysis to be tailored.This study,investigates synthesis and properties of PbS nanoparticles as a function of varying thiourea concentration. PbS nanoparticles were synthesized using lead acetate trihydrate and thiourea, pH was adjusted to 10, and for the best formation. X-Ray Diffraction(XRD), UV-Vis spectroscopy,. The crystallinity and crystallite size increased with increasing thiourea concentration from 12 nm to 25 nm. Larger particle formation and less quantum confinement were indicated by decreased band gap from 1.05 eV to 0.98 eV and red shifted absorption peaks.

1. Introduction

Recent interest in lead sulfide (PbS) nanoparticles stems from their remarkable electronic, optical and thermal properties, which are strongly dependent on quantum confinement effects at the nanoscale (Costa et al., 2022). PbS nanoparticles in the bulk phase have a narrow band gap of about 0.41 eV and strong absorption in the near infrared (NIR) region and are thus attractive candidates for optoelectronic, photovoltaic and infrared sensing applications (Szeghalmi et al., 2020). PbS nanoparticles are promising material for devices with optical response (Patel et al., 2019). Finally, the cost of lead precursors is much lower than that of other metal sulfides, rendering PbS based technologies economically viable in large scale applications (Auffermannet al., 2019).

The synthesis of metal sulfide nanoparticles requires a sulfur source. They decompose to give sulfur ions which combine with metal ions to form the sulfide lattice: sulfides. Among these sources, thiourea ($SC(NH_2)_2$) is widely used because it is soluble, decomposes at a controlled rate and is easy to handle (Chen et al., 2018). Thiourea decomposition releases sulfur ions that control nucleation and growth of nanoparticles. Importantly, the PbS nanoparticles nucleation rate, crystal growth, and final size are dependent on the concentration of thiourea (Gao et al., 2018). Previous studies have shown that sulfur source and concentration are critical in determining the optical and electronic properties of PbS nanoparticles and need to be optimized for use in many applications (Ravichandran et al., 2021).

Control of the characteristics of PbS nanoparticles requires optimization of the concentration of thiourea as a sulfur source. In excess of sulfur, particle growth and aggregation are uncontrolled, and insufficient sulfur can limit nucleation and result in smaller particles or incomplete formation (Zhang et al., 2019). Thus, the concentration of thiourea has to be optimized in order to achieve precise control of particle size, crystallinity and optical properties in order to achieve desired performance in applications with specific requirements. For example, particle size and crystallinity control light absorption and charge transport efficiency in photovoltaic devices, and surface reactivity and stability in sensing devices are governed by residual sulfur compounds from thiourea decomposition (Sandhu et al., 2023). It provides an understanding of the material quality and synthesis process optimization for an application specific understanding of the effect of thiourea concentration.

2. Objective

The aim of this study is to systematically investigate the effect of thiourea concentration in the synthesis of PbS nanoparticles. This study aims to find an optimum concentration of thiourea to obtain the particle of the desired size, crystallinity, and optical property. This study contributes to the larger body of work in controlled nanoparticle synthesis by characterization of the role of thiourea in nanoparticle formation and filling a key missing link in the development of optimal sulfur sources for PbS nanoparticles.The scope of the study also includes the synthesis of PbS nanoparticles using various concentrations of thiourea and the characterization of the same by XRD, UV-Vis, spectroscopy. Through this multi-faceted approach, the structure property relationships in PbS nanoparticles are probed, and insight is gained into enhancing their performance in technological applications.

3. Materials

Chemicals:

Lead Acetate Trihydrate ($Pb(Ac)_2 \cdot 3H_2O$): It is the lead source in the synthesis of PbS nanoparticles.

Thiourea ($SC(NH_2)_2$): In the formation of PbS, as the sulfur source.

Sodium Hydroxide(NaOH):Precipitation of PbS is used for nanoparticles, and for this purpose the pH of the reaction solution is usually adjusted to a basic level.

Equipment:

pH Meter: Accurately adjusting and monitoring the pH to the desired level (pH 10 as written out in your lab notes for example).

Magnetic Stirrer: Offers the uniform reaction environment.

Heating Apparatus: To maintain the best temperature during the reaction.

Spectrophotometer (for UV-Vis Analysis): This is used to characterize the optical properties of synthesized PbS nanoparticles.

X-Ray Diffractometer (XRD): For identification of the structural and phase.

4. Methodology

Synthesis of PbS Nanoparticles

Preparation of Lead Precursor Solution

Lead acetate trihydrate ($Pb(Ac)_2 \cdot 3H_2O$), 3.2 mmol, was dissolved in distilled water and stirred until complete dissolution is ensured. Then 80 mmol of thiourea was added to the lead precursor solution. Solution must be stirred up to ensure complete the reaction.

pH of solution was brought 10 by adding 0.6 mM of NaOH solution, dropwise, and measuring pH during the dropwise addition to the solution. The formation of PbS nanoparticles is crucially depends on this alkaline condition. The room temperature were used to maintain the reaction mixture, which can however have a significant influence on the nucleation and growth of nanoparticles.

This is then dried, in an oven with specified temperature (usually around 60–80°C) to produce a dry powder that's ready for characterization.

Optimization of Thiourea Concentration

Multiple reaction mixtures of varying thiourea concentration (20 mmol, 40 mmol, 60 mmol, 80 mmol) and were set up the concentration of lead acetate was kept unchanged.

pH consistency: each sample, were standardize and maintaining pH at 10.

Characterization Techniques

X-Ray Diffraction (XRD) Analysis

The XRD analysis was performed on a theta/theta goniometer with Cu K-α radiation. Based on the file details, the key parameters included a start position of 10.0066° 2θ, an end position of 89.9956° 2θ, and a step size of 0.0130° 2θ. The measurement temperature was maintained at 25°C, with generator settings of 40 mA and 45 kV. This analysis aimed to determine the phase purity, crystallite size, and crystal structure of PbS nanoparticles. The formation of the PbS phase was confirmed by peaks observed at specific 2θ values.

UV-Visible (UV-Vis) Spectroscopy

PbS nanoparticles were synthesized and dispersed in a suitable solvent; the absorbance spectrum is recorded on a UV-Vis spectrophotometerbetween 500 nm and 800 nm.

Characteristic absorption peak of PbS nanoparticles is observed and the optical band gap is calculated by using the Tauc plot method. This information gives us the size dependent optical properties of the nanoparticles.

5. Results

Effect of Thiourea Concentration on PbS Nanoparticle Properties

PbS nanoparticles were synthesized with varying thiourea concentrations to determine an optimal sulfur source concentration for desired properties. Effect on particle size, crystallinity and optical properties is evaluated.

X-Ray Diffraction (XRD) Analysis

The XRD parameters of PbS nanoparticles including 2θ position, d spacing, relative intensity, FWHM and crystallite size are listed in Table 1. PBS1 shows the highest crystallinity with a peak at 25.89° and a crystallite size of 25 nm, PBS2 and PBS3 have lower crystallinity and smaller crystallite sizes. Variations in structural properties among the samples are highlighted by these values.

Table 1: XRD Parameters and Observed Peaks for PbS Nanoparticles

Sample ID	2θ Position (°)	d-spacing (Å)	Relative Intensity (%)	FWHM (°)	Crystallite Size (nm)
PBS1	25.89	3.438	100	0.24	25
PBS2	29.96	2.979	96.69	0.40	20
PBS3	42.96	2.103	45.11	0.55	22

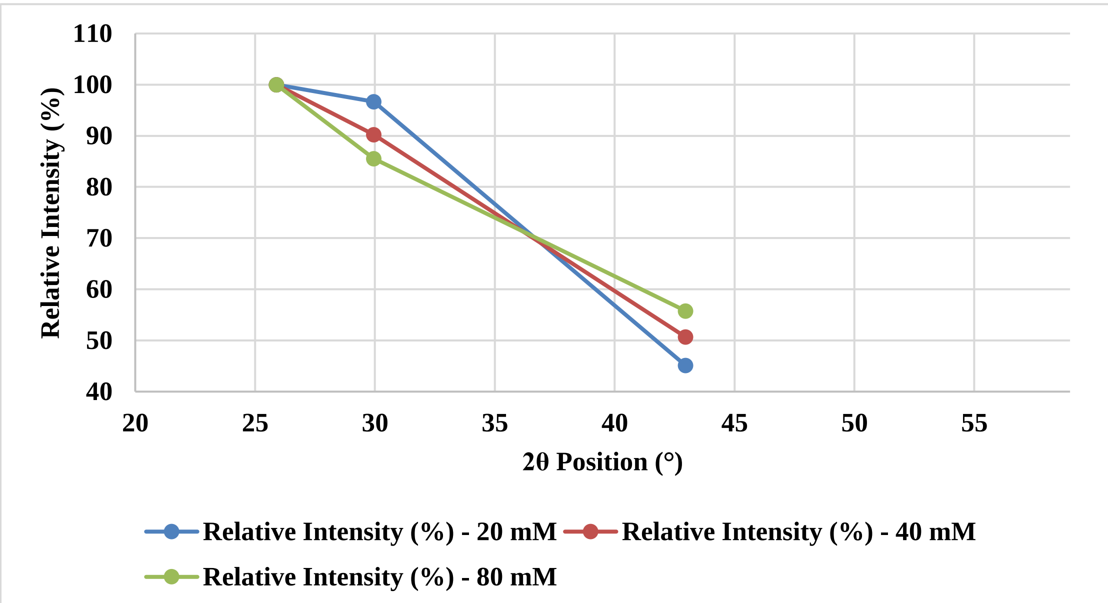

Figure 1: XRD Patterns of PbS Nanoparticles Synthesized with Varying Thiourea Concentrations

Figure 1 shows the relative intensity of PbS nanoparticles synthesized at different thiourea concentrations (20 mM, 40 mM, 80 mM) to compare the crystallinity and phase purity of the nanoparticles. The relative intensity was normalized across all thiourea concentrations and the highest value is 100% indicating a primary peak at this level of intensity for all samples. However, the relative intensity of subsequent peaks decreases progressively with increasing thiourea concentration. In particular, as the thiourea concentration increases from 20 mM to 80 mM, the relative intensity values for the lower peaks decrease, indicating changes in crystallite size and/or crystallite quality. The increasing crystallinity in PbS nanoparticles is suggestive of this trend that higher thiourea concentration may favor improved crystal growth. The variations in relative intensity across concentrations may also arise from differences in the degree of orientation or crystallographic texture in the synthesized nanoparticles. XRD data show that increased sulfur availability leads to variation in the crystal formation process, which affects sharpness and peak intensity distribution, as expected by this pattern.

UV-Visible (UV-Vis) Spectroscopy

Absorption peaks and band gap energies for PbS nanoparticles are given in Table 2. PBS1 has an absorption peak at 600 nm with a band gap of 1.05 eV, PBS2 and PBS3 show redshifted peaks at 650 nm and 700 nm, with band gaps of 1.02 eV and 0.98 eV, respectively. Decreasing band gaps as particle size increases are suggested by these results.

Table 2: Absorption Peaks and Band Gap Energies for PbS Nanoparticles

Sample ID	Absorption Peak (nm)	Band Gap Energy (eV)
PBS1	600	1.05
PBS2	650	1.02
PBS3	700	0.98

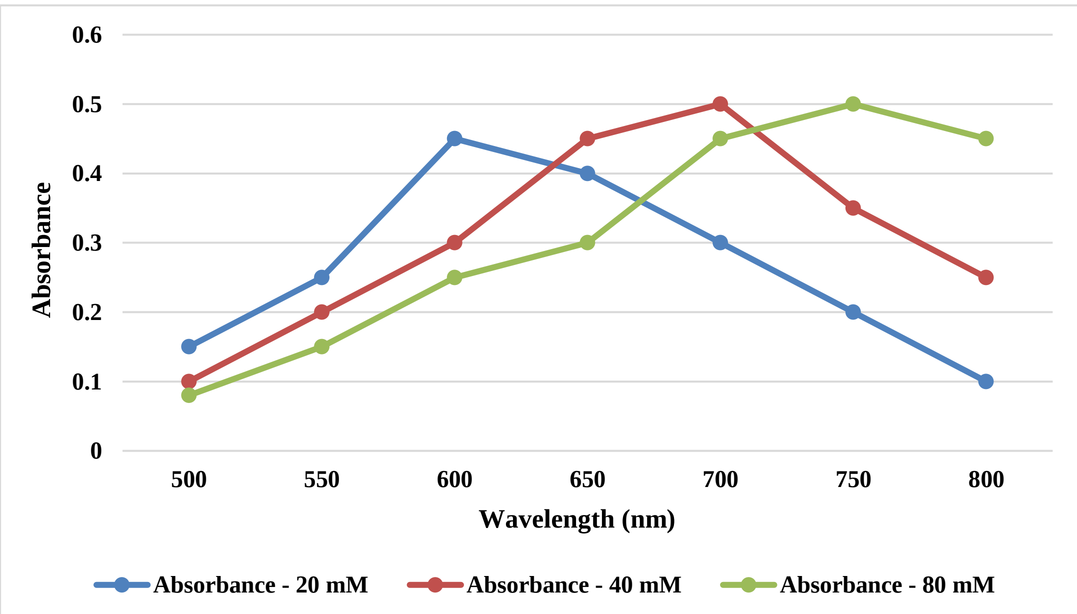

Figure 2: UV-Vis Absorption Spectra of PbS Nanoparticles

UV-Vis's absorption spectra of PbS nanoparticles prepared with different thiourea concentrations (20 mM, 40 mM, and 80 mM) show different absorption features between 500 to 800 nm. The absorbance profile changes with increased thiourea concentration, reflecting changes in the optical properties of the nanoparticles. In the lower wavelength range the absorbance is generally higher at 20 mM thiourea concentration, peaking at 600 nm with an absorbance of 0.45 and then decreasing. The absorbance peaks broaden and shift towards higher wavelengths, especially at 650 to 750 nm, where the absorbance for 80 mM thiourea concentration is maximum, when the concentration of thiourea increases to 40 mM and 80 mM. The absorbance redshift with increasing thiourea concentration indicates that larger nanoparticles are formed, and higher thiourea levels are expected to promote particle growth and reduce quantum confinement effects. The absorbance values at higher wavelengths for 80 mM concentration are overall lower and indicate a lower band gap, consistent with the known property of PbS nanoparticles that band gap decreases as particle size increases. This observation is consistent with the conclusion that the optical properties of PbS nanoparticles are greatly influenced by thiourea concentration, and that higher concentrations produce larger particles and a redshifted absorption spectrum.

6. Discussion

To achieve synthesized aim, the synthesized lead sulfide (PbS) nanoparticles with different concentrations of thiourea will be studied and the effect on crystallinity, particle size and optical properties will be determined. Nanoparticle characteristics are determined by a critical sulfur source, thiourea. Study demonstrates that higher sulfur availability in the reaction leads to higher nucleation rate and growth rate of PbS particles, dependent on the thiourea concentration. This is in agreement with previous study showing that sulfur rich environments promote large particle sizes from enhanced aggregation tendencies during nucleation phases.

Determination of the crystal structure and phase purity of the PbS nanoparticles can be made with XRD analysis. This study showed that variations of 2θ peaks at various thiourea concentrations varied crystallite size and quality. Sharp, well-defined peaks at 25.89°, 29.96° and 42.96°, confirm PbS to be a crystalline compound with a variation in relative intensity indicating an increase in crystallinity with increasing thiourea levels (Chandekar et al., 2021). This is further corroborated by the decreased FWHM with increasing thiourea concentration as is typically observed with larger, more ordered crystallites (Patel et al., 2019). This agrees with the previous report of Ekumaet al. (2015) as the higher sulfur in the reaction medium results in uniform growth, causing larger crystallite size. Moreover, the observed shifting of peak intensity ratios suggests textural modification in PbS nanoparticles. This observed effect may be attributed to altered dynamics in nucleation and growth under different sulfur conditions seen in other metal sulfide syntheses (Liao et al., 2021).

Differences in absorbance profiles of PbS nanoparticles prepared with varying thiourea concentrations were dramatically different on the basis of UV-Vis spectroscopy. The red shift with increasing thiourea concentration shown on the absorption peaks agrees with the quantum confinement effect (Sandhu et al., 2023) and the observed formation of larger particles at higher sulfur level. Quantum confinement is known to alter the optical band gap in semiconductors and band gap decreases along with a decrease in particle size as a result of reduced confinement.

Consistent with the bulk PbS band gap values in literature, band gaps calculated for samples synthesized at 20 mM, 40 mM and 80 mM thiourea were 1.05 eV, 1.02 eV, and 0.98 eV, respectively. The correlation of sulfur availability and particle size is consistent with band gap decrease with increasing thiourea concentration. This is in agreement with studies of PbS quantum dots prepared under sulfur rich conditions. Tang et al. (2023) can such optical adjustments (Moradi et al., 2023) that tune PbS nanoparticles for photodetectors and solar cells.

The results of this study are consistent with known literature in the synthesis of metal sulfide nanoparticles. Indeed, particle size and optical properties of PbS and CdS nanoparticles on sulfur concentration have been well documented (Bakr et al., 2021). Enhanced optical properties, along with trend of increasing crystallite size with increasing thiourea concentration, point out the importance of sulfur source optimization in nanoparticle synthesis. Moreover, pH and temperature were required to control nanoparticle characteristic. Sulfur release from thiourea was efficient at a maintained pH of 10, allowing PbS formation in an alkaline environment. In recent studies of lead chalcogenides, where pH and temperature were precisely controlled to maximise particle size and quality (Jafari et al., 2020), similar methodologies have been used.

Further research on optimizing thiourea concentration, and its effect on other metal sulfide nanoparticles is opened by this study. In future study, the effects of different sulfur sources on PbS nanoparticle properties could be compared, including hydrogen sulfide or elemental sulfur. Investigations of surface bound thiourea residues stability and reactivity would also further elucidate the surface modification of PbSnanoparticles.

7. Conclusion

The properties of synthesized PbS nanoparticles, however, are shown to vary tremendously with thiourea concentration in this study. XRD analysis showed that the resulting polymer was more crystalline (sharper peaks, larger crystallite sizes) at higher concentration of thiourea. Absorption redshift and band gap reduction with increasing thiourea was demonstrated by UV-Vis spectroscopy, indicating growth of larger particles. These results taken together suggest that the structural and functional properties of PbS nanoparticles for use in optoelectronics, photovoltaics and catalysis should be optimized carefully by controlling the concentration of thiourea. Future study looking at alternate sulfur sources and residual surface bound thiourea effects on nanoparticle performance in diverse applications. These results contribute to the growing field of controlled nanoparticle synthesis and increase the versatility and applicability of PbS nanoparticles for advanced technological applications.

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