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Method-Dependent Photoluminescence Behavior of CdS Nanoparticles with Varied Cd:S Ratios

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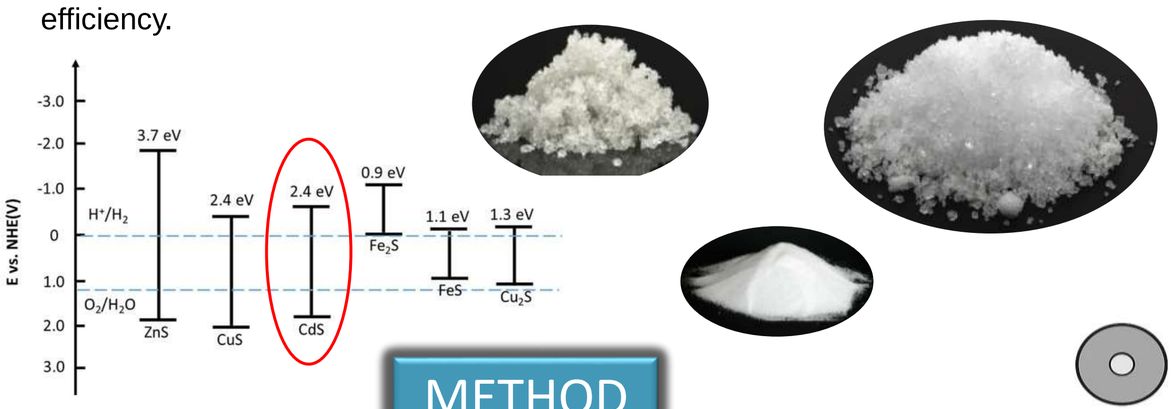
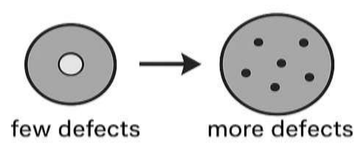
INTRODUCTION & AIM

- Cadmium sulfide (CdS) nanoparticles are direct band gap semiconductors with attractive optical and photoluminescence properties that depend strongly on synthesis method, particle size, and stoichiometry. Adjusting the Cd:S molar ratio offers an effective way to tune the crystalline phase, defect structure, and emission characteristics. In this work, CdS nanoparticles were prepared by two different approaches-successive ionic layer adsorption and reaction (SILAR) and sonochemical synthesis-using Cd:S ratios ranging from 1:0.1 to 1:1. The study aimed to establish how precursor stoichiometry and synthesis pathway influence structural transformations, band gap evolution, and photoluminescence efficiency.

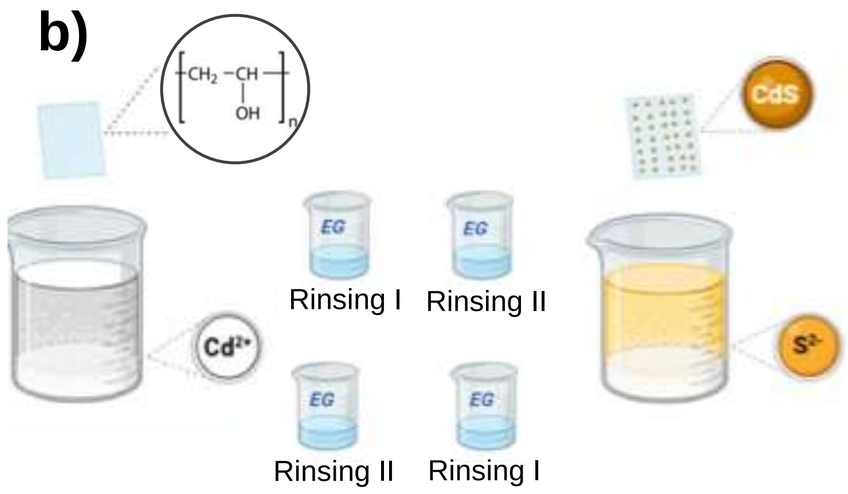




METHOD

- CdS/PVA composite films were fabricated by the SILAR technique, in which Cd^{2+} and S^{2-} ions were alternately deposited on a polyvinyl alcohol substrate for five cycles at room temperature. In parallel, crystalline CdS powders were obtained sonochemically by ultrasonic irradiation of precursor solutions under ambient conditions. Both methods were carried out with systematic variation of the Cd:S molar ratio (1:0.1, 1:0.25, 1:0.5, 1:0.75, and 1:1). Structural characterization was performed by X-ray diffraction (XRD), while optical properties were investigated by UV-Vis absorption spectroscopy and Tauc analysis for direct and indirect band gaps. Photoluminescence (PL) spectra were recorded under excitation at 330 nm. Additional analyses by FTIR and Raman spectroscopy provided insight into bonding interactions and vibrational modes.

Samples	Cd^{2+}	S^{2-}
1:0.1	1 M (2.66g)	0.1 M (0.24g)
1:0.25	1 M (2.66g)	0.25 M (0.6g)
1:0.5	1 M (2.66g)	0.5 M (1.2g)
1:0.75	1 M (2.66g)	0.75 (1.8g)
1:1	1 M (2.66g)	1 M (2.40g)



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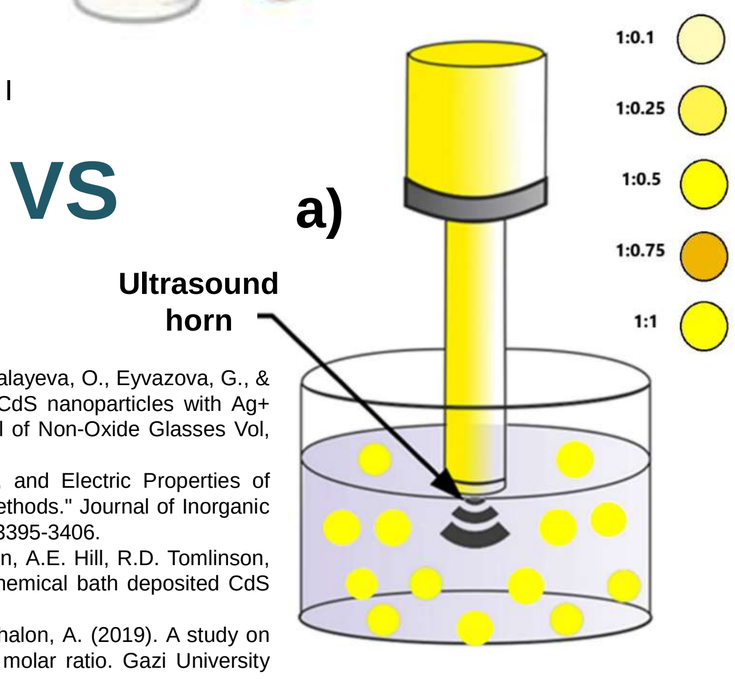
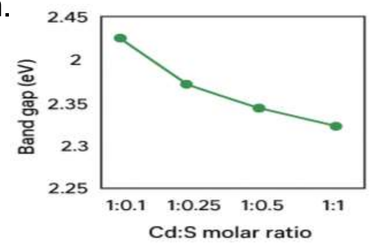


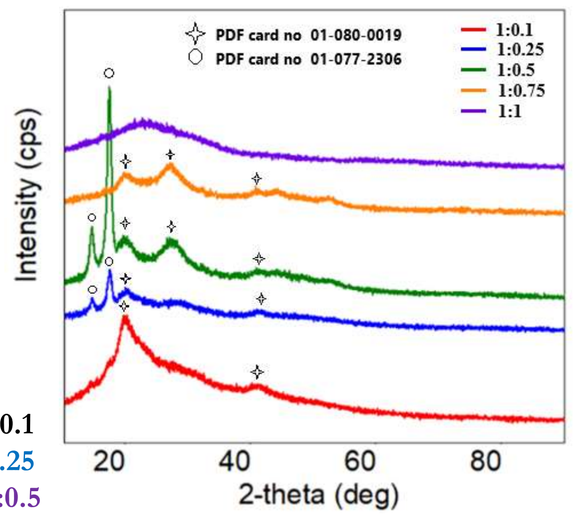
sonochemical (a) and SILAR (b) methods

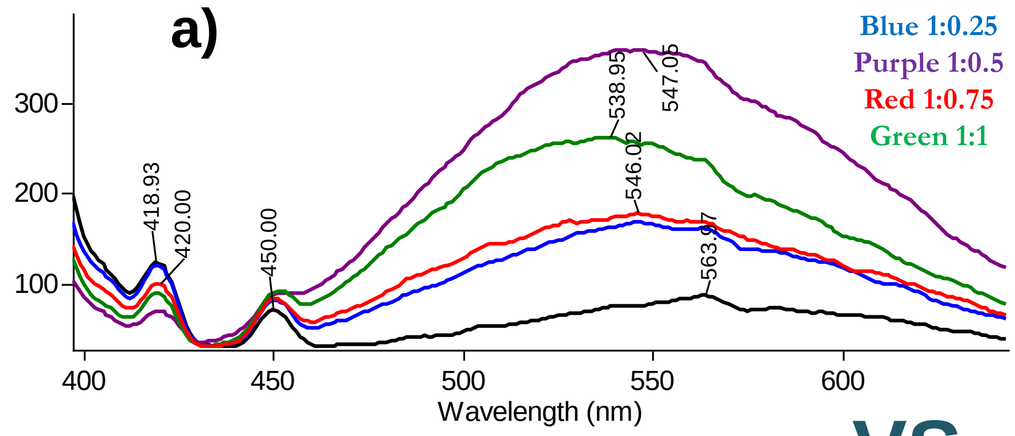
RESULTS & DISCUSSION

- ✓ XRD revealed a clear dependence of crystalline structure on the Cd:S ratio. At 1:0.1, the samples crystallized in the hexagonal phase, whereas mixed cubic–hexagonal structures were observed at 1:0.25 and 1:0.5. At the stoichiometric ratio of 1:1, the material lost long-range order and became amorphous. Optical absorption confirmed that the band gap decreased progressively with increasing sulfur concentration up to 1:0.75, followed by a slight increase in the amorphous phase. This trend is attributed to a combination of quantum confinement effects, defect state formation, and structural disorder.
- ✓ Photoluminescence analysis highlighted pronounced differences between the two synthesis methods. Sonochemically prepared CdS nanoparticles showed broad, defect-related emissions, consistent with a high density of surface and structural defects. In contrast, SILAR-grown CdS/PVA films exhibited more intense, red-shifted, and stable emission, which can be explained by exciton confinement within the polymer matrix and effective passivation of defect sites. The highest PL efficiency was recorded at the 1:0.25 Cd:S ratio, which provided an optimal balance between crystallinity and defect density. A strong emission was also observed at 1:0.75, indicating efficient excitonic recombination in this composition.



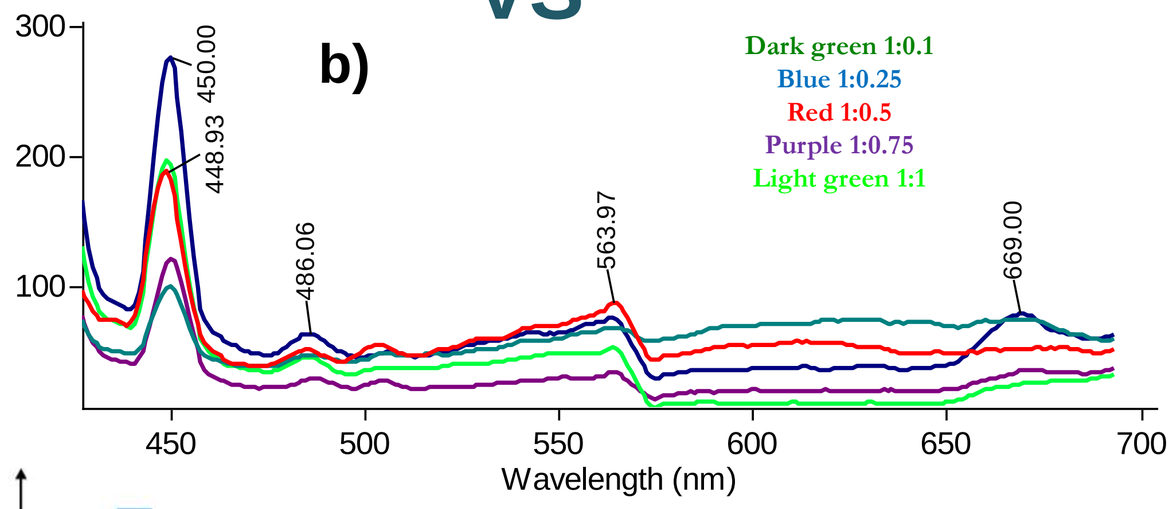
1:0.1 → **Hexagonal (wurtzite)**
1:0.25 **Mixed cubic–hexagonal**
1:0.5 → **Mixed cubic–hexagonal**
1:0.75 → **Hexagonal**
1:1 → **Amorphous**

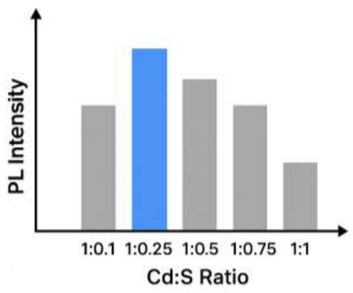




PL Spectrum at Different Cation-to-Anion Ratios measured under 330 nm excitation by sonochemical (a) and SILAR (b) method.

VS





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CONCLUSION

- ❖ The study demonstrates that both synthesis method and precursor stoichiometry critically determine the phase, band gap, and luminescence efficiency of CdS nanoparticles. The sonochemical route yields crystalline powders with broad, defect-related PL, whereas the SILAR method produces polymer-stabilized films with intense and tunable emission. Ratios between 1:0.25 and 1:0.75 were found to be optimal for achieving high photoluminescence efficiency. These findings provide a rational strategy for tailoring the structural and optical properties of CdS nanoparticles for targeted applications in optoelectronics, sensing, and photocatalysis.