



## RESEARCH ARTICLE

# Tweaking of the morphological pattern in copper sulphide nanoparticles: How does it affect the optical properties?

Sampa Mondal<sup>1</sup>, Baibaswata Bhattacharjee<sup>2\*</sup>

## Abstract

A simple wet chemical method is employed to synthesize covellite (CuS) nanostructures and different nanostructures are synthesized by varying molar ratios of copper acetate monohydrate to sodium thiosulfate pentahydrate in the starting solution. Microstructural characterizations confirm the excellent quality of synthesized CuS nanostructures having different morphology. The absorption spectra and morphology of synthesized samples change significantly with changing experimental conditions. The intensity ratio of NIR peak to UV peak, NIR peak position, and FWHM of NIR peak vary notably with the molar ratio of copper acetate monohydrate to sodium thiosulfate pentahydrate in the initial solution. The facile technique adopted in this work opens up an easy way to prepare CuS nanostructures with outstanding intensity and FWHM of NIR peak due to their unique optical properties.

**Keywords:** CuS nanostructures, UV absorption, Intensity ratio of NIR peak to UV peak, FWHM of NIR peak.

## Introduction

Copper sulfide nanoparticles (NPs) are often found in five crystalline polymorphs: chalcocite (Cu<sub>2</sub>S), djurleite (Cu<sub>1.95</sub>S), digenite (Cu<sub>1.8</sub>S), anilite (Cu<sub>1.75</sub>S), and covellite (CuS) (Andronic *et al.*, 2011). However, CuS NPs are a p-type semiconducting material that has gained popularity among researchers due to its low band gap energy (1.63-1.87 eV), size, shape, versatility, availability, stability, and non-toxic nature (Lv *et al.*, 2017; Mahanthappa *et al.*, 2019). CuS nanostructures have intriguing optical, electrical, and catalytic characteristics. These capabilities may find use in chemical sensors (Li *et al.*, 2024), switches, optical filters (V. Samuthira Pandi *et al.*, 2023), energy conversion (Parimala & Ganeshkumar, 2024),

biological labeling (Roy *et al.*, 2024), laser light monitoring (Kumar *et al.*, 2023), DNA detection (Huynh, 2020), and photodegradation of contaminants (Yasmin *et al.*, 2021). Photothermal ablation is one of the most important applications of CuS nanostructures and this property depends on NIR absorption of CuS nanostructure (Chen *et al.*, 2019). To enhance the photothermal ablation ability of CuS nanostructures in the presence of NIR light, enhancing the NIR peak intensity and FWHM of the NIR peak is very important.

A simple, low-cost wet chemical method has been used to synthesize CuS nanostructures and different samples are synthesized with changing molar ratios of copper acetate monohydrate to sodium thiosulfate pentahydrate. Regulating the intensity and FWHM of the NIR peak of CuS nanostructures by varying molar ratios of copper acetate monohydrate to sodium thiosulfate pentahydrate is the focus of this research. To the best of our knowledge, this is the first report on tailoring the NIR absorption of CuS nanostructures by varying molar ratios in the starting solution. The morphology and absorption spectra of CuS nanostructures vary with changing molar ratios in the starting solution. Additionally, remarkable changes in the intensity ratio of NIR peak to UV peak, NIR peak position, and FWHM of NIR peak with the molar ratio of copper acetate monohydrate to sodium thiosulfate pentahydrate are investigated. CuS nanoparticles' infrared absorption as a semiconductor is essentially distinct from that of gold nanostructures (Roper *et al.*, 2007). Whereas

<sup>1</sup>Department of Physics, Bankura Zilla Saradamani Mahila Mahavidyalaya, Bankura, West Bengal, India.

<sup>2</sup>Department of Physics, Ramananda College, Bishnupur, Bankura, West Bengal, India.

\***Corresponding Author:** Baibaswata Bhattacharjee, Department of Physics, Ramananda College, Bishnupur, Bankura, West Bengal, India, E-Mail: baib23@gmail.com

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**Table 1:** Design of experiment for the formation of different CuS nanostructures and sample name of different CuS nanostructures according to the experimental conditions

Sample Name	CuS-1	CuS-2	CuS-3	CuS-4	CuS-5	CuS-6
Copper acetate monohydrate (g)	4.39	4.39	4.39	4.39	4.39	4.39
Sodium thiosulphate pentahydrate (g)	3.89	4.19	4.54	5.45	6.06	6.82
Molar ratio (copper acetate monohydrate/sodium thiosulphate pentahydrate)	1.4	1.3	1.2	1	0.9	0.8

surface plasmons are responsible for the absorption from gold nanostructures, the former is formed from energy band-band transitions (Kwon *et al.*, 2019). However, this investigation offers a simple and easy way to regulate the NIR region of CuS nanostructures. Because of its unique optical characteristics, CuS nanostructure can be used in the medical field to stimulate the growth of cancer cells in the presence of NIR light.

## Materials and Methods

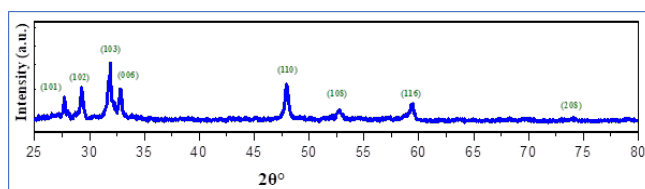
### Synthesis of CuS NPs

At first, following the experimental design, 4.39 g of copper acetate monohydrate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) (Sigma-Aldrich, purity 99.99%) is dissolved in 250 mL of deionized (DI) water (Merck, purity 99.99%) under continuous stirring at room temperature (as shown in Table 1). Separately, 3.89 gm of sodium thiosulphate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) (Sigma-Aldrich, purity 99.99%) is dissolved in 250 mL of DI water as displayed in Table 1. After that,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution is mixed dropwise into the  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  solution at 90°C. The resulting greenish-black solution is stirred for an additional 4 hours at 90°C. This solution is then filtered to obtain the precipitates, which are washed four times with DI water. The precipitates are then dried at room temperature until they become completely dry. To obtain the samples in the form of fine powder, finally, the samples are grounded.

Keeping the amount of copper acetate monohydrate (4.39 g) the same, the amount of sodium thiosulfate pentahydrate is changed to 3.89, 4.19, 4.54, 5.45, 6.06, and 6.82 g to vary the molar ratios (1.4, 1.3, 1.2, 1, 0.9, and 0.8) (Table 1). Different CuS nanostructures are prepared using the same procedure according to Table 1 to obtain copper-rich through stoichiometric to sulfur-rich samples.

### Characterizations and Instrumentations

Using a Bruker D8 Advance diffractometer, the crystallinity of the CuS NPs is assessed throughout an angular range ( $2\theta$ ) of 20 to 80°. A Zeiss Sigma field-enhanced secondary electron

**Figure 1:** XRD patterns of ZnO-1

microscope (FESEM) is used to examine the morphology of the produced ZnO NPs. A Jasco V-770 spectrophotometer is used to record absorption spectra spanning the wavelength range of 300 to 1100 nm.

## Result and Discussion

### X-ray Diffraction

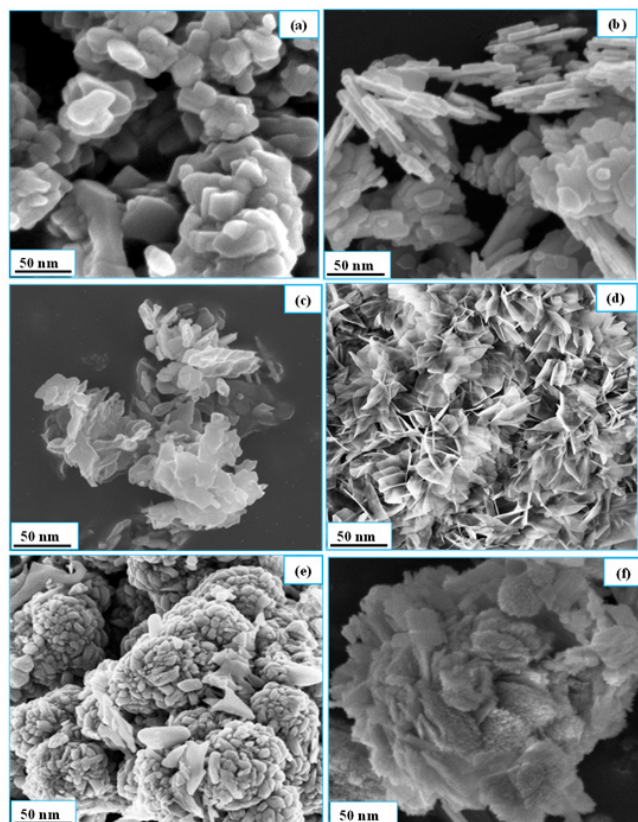
The X-ray Diffraction (XRD) spectra of CuS-1 are shown in Figure 1 as a representative. As demonstrated by the XRD patterns in Figure 1, the sample exhibits common peaks located at  $2\theta$  positions of 27.67°, 29.45°, 31.28°, 32.55°, 47.64°, 52.84°, 59.47°, 73.94° which are attributed to the crystal planes 101, 102, 103, 006, 110, 108, 116, respectively, confirming the hexagonal crystal structure of the CuS-1 (Iqbal *et al.*, 2020). XRD spectra of the other CuS nanostructure do not show any extra peak, indicating the same hexagonal crystal structure of the other samples.

### Morphological Study

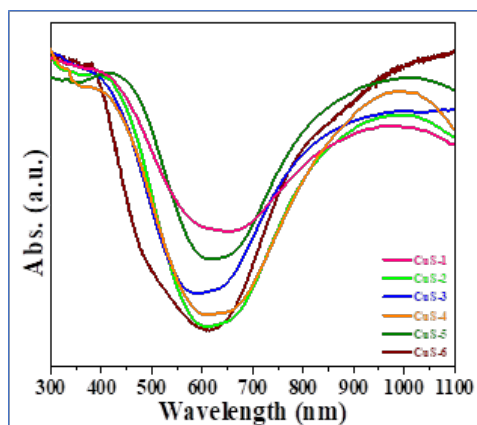
The morphological pattern of the CuS NPs is investigated using FESEM images. The FESEM images of the CuS nanostructure are displayed in Figure 2. Different samples are synthesized from copper-rich through stoichiometric to sulfur-rich conditions by varying molar ratios of copper acetate monohydrate to sodium thiosulfate pentahydrate (at 1.4, 1.3, 1.2, 1, 0.9, and 0.8) in the starting solution. Owing to this experimental design, the morphological patterns of synthesized samples are found to change significantly. Stirring at a temperature of 90°C promotes the homogeneous formation of CuS crystalline nuclei and then these CuS nanoparticles are self-assembled to generate different morphology of CuS nanostructure according to the experimental design. At molar ratios (copper acetate monohydrate to sodium thiosulfate pentahydrate) 1.4, 1.3, 1.2, 1, 0.9 and 0.8 the structures of synthesized samples are nanocube, nanoplate, nanopetal, nanoflake, nanosphere, and nanoflower, respectively (Figure 2).

### Optical Studies

The board absorption spectra throughout the UV-Vis-NIR region of the synthesized CuS nanostructures under different experimental conditions are shown in Figure 3. The line shapes of the UV-vis absorption spectra change significantly with changing molar ratios (at 1.4, 1.3, 1.2, 1, 0.9, and 0.8) of copper acetate monohydrate to sodium



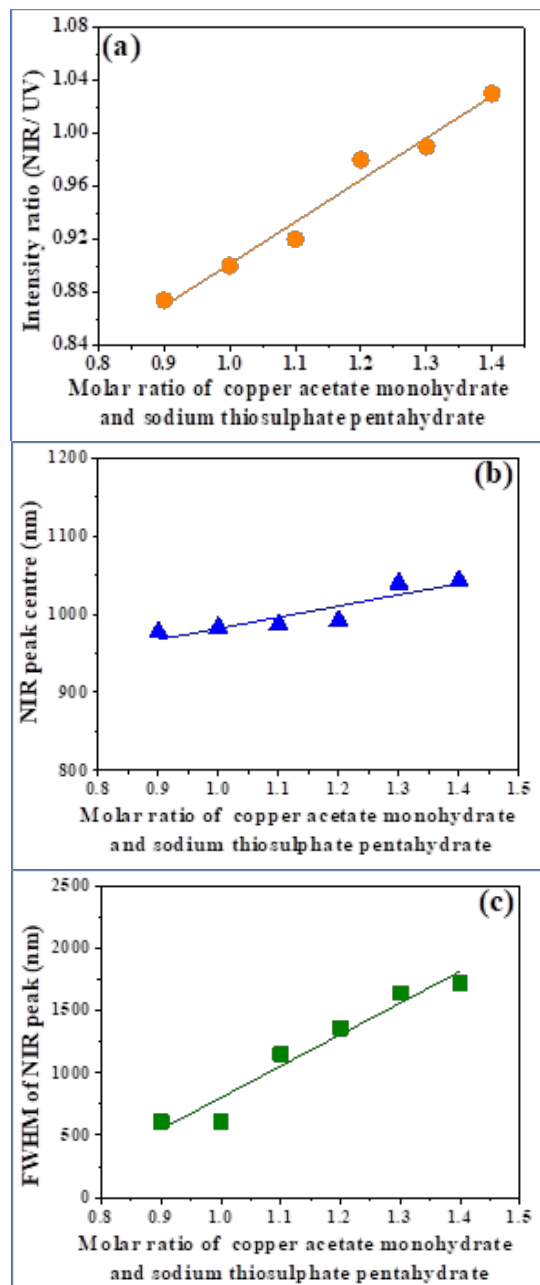
**Figure 2:** FESEM images of all nanostructures with different experimental conditions: (a) CuS-1 (nanocube), (b) CuS-2 (nanoplate), (c) CuS-3 (nanopetal), (d) CuS-4 (nanoflakes), (e) CuS-5 (nanosphere), (f) CuS-6 (nanoflower)



**Figure 3:** UV-vis absorption spectrum of CuS nanostructures with different experimental conditions

thiosulfate pentahydrate in the starting solution. In addition to that, changes also can be noticed in the absorption bands that appear in the NIR region, which is the characteristic feature of CuS nanostructures (Ayodhya *et al.*, 2016). The formation of the broad NIR absorption band in CuS nanoparticles can be attributed to the intra-band transition and surface plasmon resonance (Beynis, 2021).

The variation in the ratio of absorption intensity of NIR to UV absorption bands with the molar ratio of copper



**Figure 4:** Changes of optical properties with molar ratio of copper acetate monohydrate and sodium thiosulfate pentahydrate in the starting solution: (a) Changes of the intensity ratio of NIR peak to UV peak with molar ratio, (b) Changes of NIR peak center with the molar ratio, (c) Changes of FWHM of NIR peak with molar ratio

acetate monohydrate to sodium thiosulfate pentahydrate is given in Figure 4a. Figure 4a shows this value is highest for CuS-6. Moreover, the shift in the NIR peak center with the experimental design is given in Figure 4b. The maximum NIR peak center is seen for CuS-6 (Figure 4b). In addition, the variation of the FWHM of the NIR peak with the molar ratio of copper acetate monohydrate and sodium thiosulfate pentahydrate is displayed in Figure 4c. Figure 4c shows that the FWHM of the NIR peak is greatest for CuS-6.

## Conclusion

A simple and low-cost wet chemical method has been used to produce high-grade, pure, highly crystalline CuS nanostructures and different samples (copper-rich to sulfur-rich samples) are synthesized with changing molar ratios of copper acetate monohydrate to sodium thiosulfate pentahydrate in the initial solution. SEM and XRD investigations confirm that excellent CuS nanostructures are produced. The simple approach used in this study makes it possible to produce easily CuS nanostructures with amazing NIR absorption. With varied molar ratios in the starting solution, the UV-vis spectra and morphology of the CuS nanostructure display interesting and remarkable changes. However, the intensity ratio of the NIR peak to UV peak, NIR peak center, and FWHM of the NIR peak varies significantly with experimental design. The greatest intensity ratio of the NIR and UV peak is seen for ZnO-6. In addition, the position of the NIR peak center and FWHM of the NIR peak are highest for CuS-6. So, these CuS nanostructures interacting with NIR light may be used to stimulate the growth of cancer cells and solar heaters. Thus, our study also offers a simple and easy way to regulate the NIR region of the CuS nanostructure.

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