

## LOW TEMPERATURE SYNTHESIS OF L-CYSTEINE CAPPED Cu<sub>2</sub>Se QUANTUM DOTS

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Quantum dots have already proven features that can be considered to improve their properties for biological applications. Metal selenide nanoparticles possess semiconducting behaviors that can vary with their structural and optical properties evolving from their synthesis. The copper selenide nanoparticles have been synthesized by aqueous medium through a simple, non-toxic and environmentally friendly colloidal route. The FTIR spectroscopy confirmed the binding of cysteine onto the surface of the nanoparticles via the thiol group. The XRD patterns revealed cubic phase structures of the Cu<sub>2</sub>Se nanoparticles synthesized at different temperatures. The optical absorption as a function of wavelength for the prepared Cu<sub>2</sub>Se nanoparticles at different temperature was also investigated. The morphology of the nanoparticles changed from spherical to nanorods as the reaction temperature was increased.

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### 1. Introduction

In the past decades, chalcogenide semiconductor nanocrystals (NCs) have attracted tremendous attention due to their unique shape- and size-dependent physical and chemical properties, which cannot be obtained from their bulk counterparts [1–4]. Their properties are strongly influenced not only by the composition and structure of the matrix, but also by the preparation method. Semiconductor nanocrystals have been applied in various fields, including biological labelling and diagnostics, light emitting diodes, photovoltaic devices, and lasers [5–9].

Copper selenide is a p-type I-VI semiconductor that has gained particular interest due to the excellent optical, electronic and electrical properties [10–11]. It has numerous phases and structural forms: stoichiometric (CuSe, Cu<sub>2</sub>Se, CuSe<sub>2</sub>, Cu<sub>3</sub>Se, Cu<sub>5</sub>Se<sub>4</sub>, Cu<sub>7</sub>Se<sub>4</sub>, etc.) and nonstoichiometric (Cu<sub>2-x</sub>Se). It can be constructed into several crystallographic forms (monoclinic, cubic, tetragonal, hexagonal, etc.) with their bulk materials possessing band gap energies between 1-2.3 eV [12–13]. A number of methods have been adopted to synthesize Cu<sub>2</sub>Se, such as gamma irradiation [14], microwave assisted heating [15] and sonochemical method [16–17]. Copper selenide can be synthesized through a chemical reaction technique which has many advantages such as simplicity, no requirement for sophisticated instruments, non-toxic, low-cost and the potential for large-scale production. In this paper, we report the synthesis and characterization of Cu<sub>2</sub>Se nanoparticles capped with hydrophilic ligand containing multi-functional moieties. The influence of reaction temperature is also investigated. The synthesized Cu<sub>2</sub>Se nanoparticles were characterized by UV-Vis spectroscopy, Photoluminescence spectroscopy (PL), Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM).

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## 2. Experimental

### 2.1 Reagents

Copper chloride ( $\text{CuCl}_2$ ), sodium selenite ( $\text{Na}_2\text{SeO}_3$ ), L-cysteine amino acid ( $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ ), sodium borohydride ( $\text{NaBH}_4$ ), sodium hydroxide ( $\text{NaOH}$ ) were purchased from Sigma-Aldrich. All chemicals were used as purchased without further purification.

### 2.2. Preparation of selenium source

Selenium source was prepared by dissolving 0.05 M of  $\text{Na}_2\text{SeO}_3$  (0.5g) with 2.0 M  $\text{NaBH}_4$  (0.3783g) in 50 ml distilled water which is taken in 100 ml beaker. The solution was stirred for 20 minutes until the brown solution forms that indicates the reduction of selenium.

### 2.3. Preparation of L-cysteine-capped $\text{Cu}_2\text{Se}$ nanoparticles

Cysteine-capped  $\text{Cu}_2\text{Se}$  nanoparticles were synthesized using one-pot synthetic approach directly in an aqueous medium. A solution of 0.2 M  $\text{CuCl}_2$  (0.5g) in distilled 20 ml water was prepared at room temperature. A 30 ml of 0.2 M solution of L-cysteine was added into the  $\text{CuCl}_2$  solution with a constant stirring until the mixture became turbid white. The pH of the solution was adjusted to from 5 to 11 by adding few drops of freshly prepared 1 M  $\text{NaOH}$  solution, which turned the solution transparent again. The desired quantity of the prepared Se source (here  $\text{Cu}^{2+}:\text{Se}^{2-}$  is maintained 1:1) was added dropwise. The mixture has been refluxed for 1 h at 55, 75 and 95 °C. The formation of blue to black precipitate was observed which indicate the formation of  $\text{Cu}_2\text{Se}$  nanoparticles. The particles were cleaned three times with acetone. Water-soluble  $\text{Cu}_2\text{Se}$  nanoparticles were collected for further characterization.

### 2.4. Physical measurements

The optical properties of the materials were determined by placing the water dispersion of the nanoparticles into quartz cuvettes (1 cm path length) using distilled water as a solvent. The PG Instruments Ltd T80+ UV-vis spectrometer was used to carry out the absorption measurements. Emission spectra of the particles were recorded on a JASCO spectrofluorometer FP-8600 spectrometer with a xenon lamp at room temperature. Infrared spectra of the nanoparticles were recorded on PerkinElmer spectrum 400 FT-IR spectrometer ranging from 500 to 4000  $\text{cm}^{-1}$ . The samples were placed onto the universal ATR sample holder and pressed on top by gauge force arm. X-ray diffraction (XRD) patterns of powdered samples were carried out on Bruker D8 advance using a Co (1.78898 nm) radiation source operating at 40 kV, for  $2\theta$  values over 20 – 80 °. The morphology of nanoparticles was determined by Technai G<sup>2</sup> TEM spirit operated at 200 kV. Transmission electron microscopy (TEM) samples were prepared by drop-casting the nanocrystal dispersion in distilled water onto the carbon-coated copper grids and allowed to dry at room temperature.

## 3. Results and discussion

UV-vis absorption spectra of synthesized copper selenide nanoparticles are shown in Fig. 1(I). The nanoparticles absorption band edges showed quantum confinement resulting from the blue shift from the bulk's 1180 nm. The spectra revealed the absorption bands at 440, 435, and 420 nm for the temperatures of 55, 75, and 95 °C, respectively. According to the absorption analysis, the nanocrystals obtained at different temperatures displayed similar optical properties. However, as the temperature was increased, there was a slight blue-shift of the band edge was observed. The Tauc plot band edges for the samples prepared at the temperature of 55, 75, and 95 °C in Fig. 1(II) were located at 3.23, 3.50, and 3.70 eV, respectively.

The emission maximum for samples in Fig. 1(III) (a) & (b) for nanoparticles synthesized at 55 and 75 °C were located at about 438 and 434 nm with FWHM at 62 and 61 nm respectively, while Fig. 1(III) (c) shows the maximum at 421 nm with FWHM at 32 nm. The full width at half maximum (FWHM) is reduced which could be attributed to the polydispersed distribution. The broad peaks observed on PL spectra at 55 and 75 °C indicate monodispersity of the particles.

However, the sample synthesized at 95 °C displayed polydispersity approach. This observation agrees with absorption analysis as observed at 55 and 75 °C which could exhibit similar properties, while sample synthesized at 95 °C poses distinctive features.

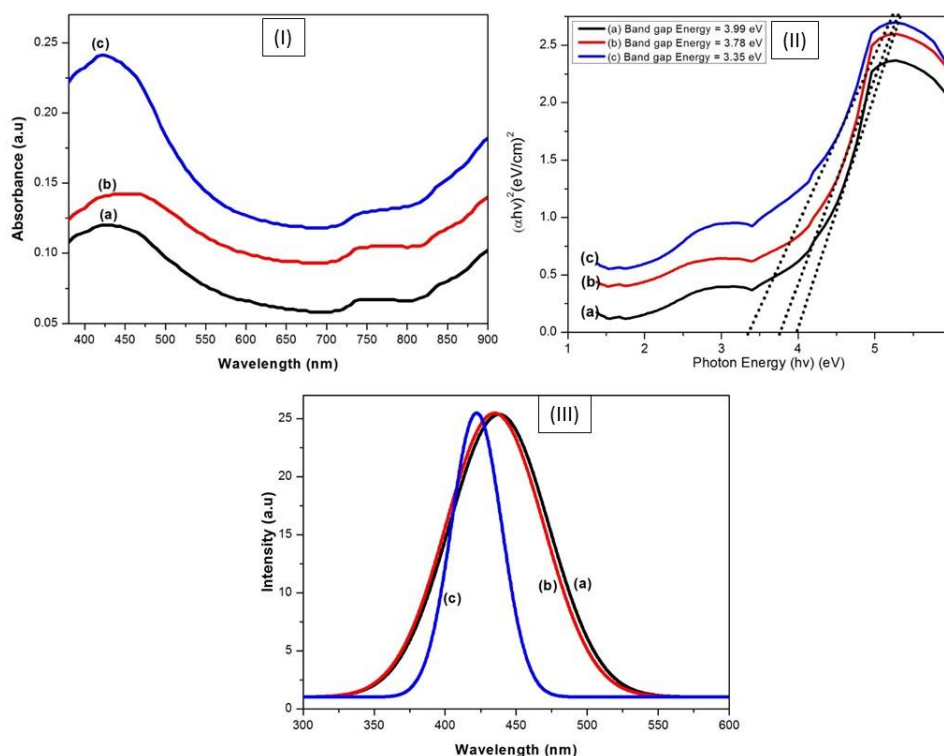


Fig. 1. Absorption spectra (I), its corresponding Tauc Plot (II), and emission (III) spectra of L-cysteine-capped  $\text{Cu}_2\text{Se}$  nanoparticles synthesized at (a) 55, (b) 75, and (c) 95 °C.

The FTIR spectra was done to study the interaction of cysteine with the surface of the nanocrystals. The spectra of free L-cysteine and L-cysteine-capped  $\text{Cu}_2\text{Se}$  nanoparticles synthesized at 95 °C are shown in Fig. 2(I). The IR bands around  $1550\text{-}1600\text{ cm}^{-1}$  (*sv*  $\text{COO}^-$ ),  $1400\text{ cm}^{-1}$  (*mv*  $\text{COO}^-$ ), and  $3500\text{-}3000\text{ cm}^{-1}$  (*mv* OH, COOH), indicate the presence of carboxylic group. The peaks at  $2900\text{-}3420\text{ cm}^{-1}$  (*mv* N-H),  $600\text{-}800\text{ cm}^{-1}$  (*mv* C-S) and at  $2550\text{-}2750\text{ cm}^{-1}$  (*mv* S-H) indicate the presence of  $-\text{NH}_2$ , C-S and  $-\text{S-H}$  groups respectively, while the peak. There are coexisting bands of  $-\text{COO}^-$ ,  $-\text{NH}_2$  observed on both L-cysteine and L-cysteine-capped  $\text{Cu}_2\text{Se}$  QDs. Therefore, carboxylic acid and the amino group are present on the surface. The S-H group vibration ( $2550\text{-}2670\text{ cm}^{-1}$ ; *wv* S-H) is absent on the surface of the L-cysteine-capped  $\text{Cu}_2\text{Se}$  QDs due to the formation of covalent bonds between thiols and the surface of  $\text{Cu}_2\text{Se}$ .

The XRD pattern of the synthesized materials from different reaction temperatures are shown in Fig. 2(II). The XRD pattern showed that the yielded particles were indeed copper selenide. The diffraction patterns of the synthesized nanoparticles show four diffraction peaks that were well defined at  $32.11^\circ$ ,  $53.13^\circ$ ,  $63.37^\circ$ , and  $78.24^\circ$ , which were indexed to (111), (220), (311), and (400) reflection planes of the cubic structure of  $\text{Cu}_2\text{Se}$  (JCPDS File No: 01-088-2045), respectively. The lattice parameters were calculated from the XRD patterns and found to be  $a = b = c = 4.864\text{ \AA}$ . The sharpness of the peaks observed from particles synthesized at 75 and 95 °C suggests highly crystalline nanoparticles compared to those at 55 °C and the position of the peaks matched perfectly with the standard  $\text{Cu}_2\text{Se}$  with no detection of impurities.

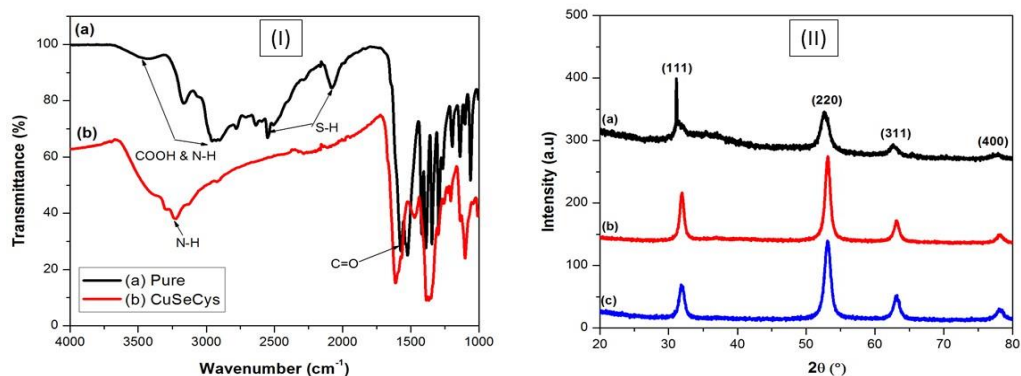


Fig. 2. The FTIR spectra of (a) free L-cysteine, (b) L-cysteine-capped Cu<sub>2</sub>Se nanoparticles synthesized at 95 °C (I), XRD patterns of L-cysteine-capped Cu<sub>2</sub>Se nanoparticles prepared at (a) 55, (b) 75, and (c) 95 °C (II).

The TEM images of all synthesized copper selenide nanoparticles and the corresponding size distributions are shown in Fig. 3. The nanoparticles were in various shapes dominated by rods phase. The diameters of particles synthesized at 55, 75, and 95 °C were  $1.33 \pm 0.367$  nm,  $4.79 \pm 0.78$  nm and  $4.95 \pm 0.718$  nm respectively. The particles synthesized at 55 °C (Fig. 3(a)) were smaller with a better Gaussian curve and narrower size distribution (standard deviation of 0.367) than those synthesized at higher temperatures. It was observed that when the temperature increased, the morphology changes from spherical to nanorods like structures.

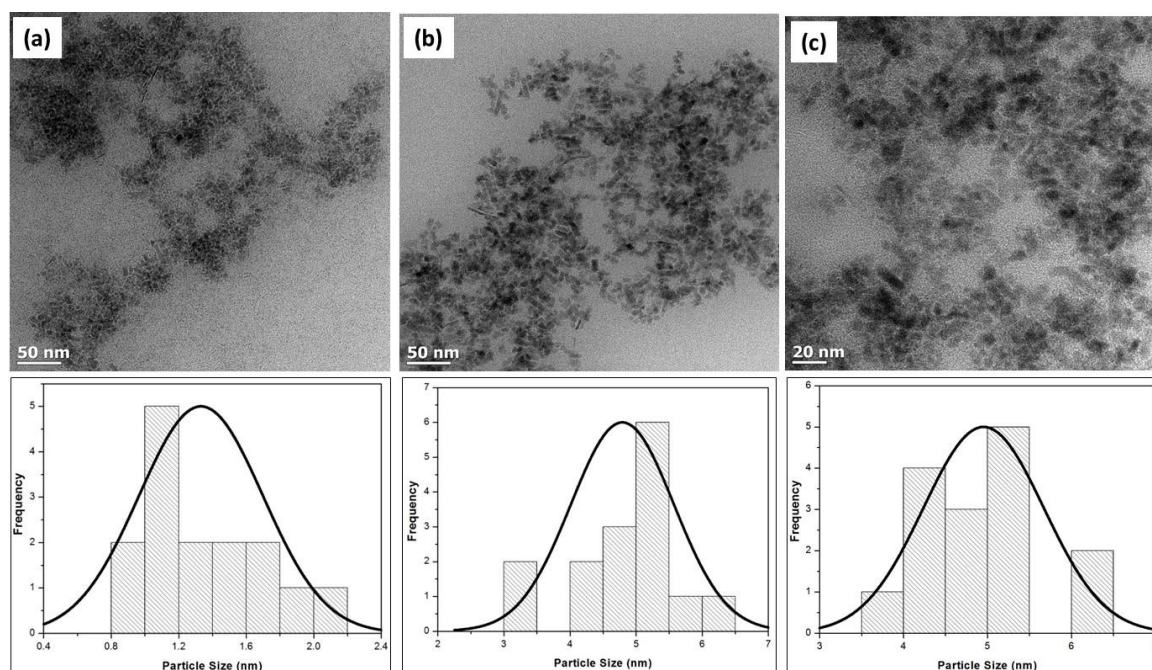


Fig. 3. TEM images and size distribution curve of L-cysteine-capped Cu<sub>2</sub>Se nanoparticles prepared at (a) 55, (b) 75, and (c) 95 °C.

#### 4. Conclusion

Copper selenide nanoparticles have been synthesized by the aqueous medium through a simple, non-toxic and environmentally friendly colloidal route. Cysteine as a stabilizing agent and

the temperature are important parameters that determined the final morphology of the nanoparticles. The FTIR spectral analysis revealed that thiol moiety have a slight covalent bond to the surface of Cu<sub>2</sub>Se. TEM revealed mixed spherical and nanorods shaped Cu<sub>2</sub>Se nanoparticles with highest temperature yielding largest number of rods.

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