Effect of Growth Condition on the Structural, Optical and Ionic Characteristics of Chemically Synthesized CuS Nanostructures in Starch Matrix

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Abstract. Spindle-shaped CuS nanoparticles of sizes 3–13 nm dispersed in starch were synthesized using copper acetate monohydrate (\text{Cu(CH}_3\text{COO)}_2\) and thiourea (\text{SC(NH}_2\text{)}_2\) as precursors via a green biocompatible chemical route. The structure indicated a possible phase change from covellite to djurleite under different growth conditions. Absorption spectra showed good quantum confinement of CuS in starch matrix with an enhancement of the band gap 2.8–3.85 eV. The photoluminescence (PL) spectra exhibited a strong UV-Vis.-blue emission in the ranges 362–395 nm and 398–471 nm with excitation wavelengths of 325 nm and 350 nm respectively along with some weak green emissions. Ionic contributions of the electrolytic ionic CuS solution as measured by a standard conductivity cell clearly showed the semiconducting behavior of the product material. The activation energies were in the range 0.1007–0.1602 eV. The ionic properties of the ionic CuS solution were correlated with molar concentration of the host material. Studies have shown that ionic CuS solutions behave as weak electrolytes dispersed in starch and may be potentially exploited as mixed ionic electronic conductors in electrochemical technology. The excellent optoelectronic properties of the as synthesized material may also be utilized in different optoelectronic devices such as UV-Blue LEDs.

Key Words: Biocompatible, blue-shift, ionic conduction, green emission, nanoparticles, quantum confinement.
1 Introduction

Copper sulphide nanomaterials exhibit novel structural, optical and electrical properties owing to quantum size effects and surface effects. Most significantly, these properties are quite different from those of their bulk materials. Nanosize CuS shows size tunable physical as well as optoelectronic properties depending on different growth conditions which have extensively been utilized in different optoelectronic device applications [1, 2]. Nanoscopic copper sulphide is a promising p-type IB-VIA group semiconducting material with high absorption coefficient (10^4 cm\(^{-1}\)) and a direct band gap 2.5 eV for bulk hexagonal structure possessing high mobility of copper ions [3–5]. The p-type metallic conduction of CuS may be as a result of deficiency of delocalized electrons in the top of valance band (holes in S (2p) valance band) relative to close shell configuration [6]. Copper sulphide exists in various sub-stoichiometric compound forms such as CuS, Cu\(_{1.96}\)S, Cu\(_{1.8}\)S, Cu\(_{2}\)S\(_{4}\) and CuS\(_{2}\) with different phases and crystal structures. The covellite (CuS) phase exhibits superconductivity at 1.6 K [7–9]. The amorphous brown chalcocite (Cu\(_{2}\)S) and the green-black crystalline covellite (CuS) phases have got special attention among the researchers because of their metal-like electrical behaviors [10–12]. CuS nanoparticle exhibits strong emission and absorption ability in the UV-Vis. region (300 nm-800 nm) which can therefore be potentially utilized in different optoelectronic device applications [13]. Owing to high surface to volume ratio, surface states as well as oxidation states of copper ions in CuS play a key role in determining the photoluminescence (PL) properties of the material. Growth temperature, molar concentrations and volumetric compositional ratio of the precursors, capping material and complexing agent also enormously affect in controlling stability, structural uniformity and shape and size of the nanoparticles. Another interesting property of copper sulphide nanomaterial is that electrolytic ion CuS solution exhibit temperature dependent semiconducting behavior as well as fast ion conduction at high temperature [14] thus transferring ionic contributions towards electrical properties of the material. These optoelectronic properties of the nanostructure CuS have potential applications in optoelectronic devices ranging from light emitting diodes to solar cells and electrochemical technologies such as in battery electrodes, fuel-cell electrodes, membrane reactors, etc. Further, owing to existence of residual strains in the material, nanostructure CuS exhibits lattice distortions [15]. As consequences, the structural parameters of the material such as lattice constant, crystalline quality, grain-size, dislocation density, micro-strain etc. are strongly influenced by the growth parameters. Thus from application point of view, investigation on the growth conditions is highly desirable.

Traditionally, CuS nanoparticles are synthesized both by solid state reaction and solution synthetic routes. There are numerous reports to synthesize copper sulphide nanoparticles of different shape and size. Few of them are chemical
bath deposition, chemical vapor deposition, spray pyrolysis, hydrothermal and solvothermal synthesis, green chemical synthesis route etc. Such synthetic techniques however require very high sophisticated instruments to achieve different growth conditions specially the high temperature. Besides, they are toxic, costly and hazardous for environment. Here, we report a green chemical synthesis route which is simple, nontoxic, cost effective, environmentally friendly, bio-compatible and easy to handle. We used a good green bio-polymer starch as capping material which is nontoxic and eco-friendly having different functional groups including –OH group in its structures. The –OH group of amylopektin, an ingredient in starch is expected to play a crucial role to obtain uniform structure as well as to prevent agglomeration or faster growth of the nanoparticles. This type of polymer was also used by others [16]. In literature, most studies emphasized on different growth parameters for synthesis of nanoparticles. Most researchers reported synthesis of CuS nanoparticles of various sizes and shapes and found an increase in band gap of copper sulphide on decreasing molar concentration [17]. We got an enhancement of band gap 2.8–3.85 eV on lowering molar concentration of the precursors. Thus, the size of nanoparticles decreases with lowering molar concentration. The ionic conductivity of CuS as well as the activation energy of the mobile ions is found to depend on temperature of the ionic solution. This is in good agreement with others [18]. A. Jamie et al observed increase of ionic conductivity with increase of relative humidity of the sample [19]. CuS samples with larger band gaps exhibited lower ionic conductivity which agreed well with reported literature [20]. Investigation of ionic conductivity in an ionic solution that we reported here, though the chemistry involved merits further study suited well in determining electronic properties of CuS nanoparticles. Further, the approach is simple and requires low cost infrastructures. Thus, we employed a simple, eco-friendly, solution processable, scalable, stable and inexpensive chemical route to synthesize copper sulphide nanoparticles in a green aqueous solution. Despite all the advantages of this synthetic route, synthesis of high quality CuS nanoparticles with phase purity, crystalline quality, structural uniformity and controlled state of agglomeration in an eco-friendly and inexpensive manner has still been posing a challenge for the research community. Keeping the above aspects in view, we undertook this experimental work and presented the findings in this article.

In this study, we report the effect of molar concentration of precursors in determining various copper sulphide nanostructures governed by quantum confinement effect. The temperature dependent photoluminescence properties of the synthesized nanoparticles and the optoelectronic properties of ionic copper sulphide nanoparticles in different molar solutions in an ambient atmosphere have been discussed. The role of starch as a capping material and ammonia (aq.) as a complexing agent in the confinement process has been elucidated. Structural, optical and ionic parameters are also correlated with different growth parameters. Details have been discussed in appropriate sections.
2 Experimental

2.1 Materials and methods

Analytical grade chemicals from Merck were purchased and used without further purification for all the synthesis processes. 

\[ \text{Cu(OAc)}_2 \left( \text{(CH}_2\text{COO)}_2\text{Cu.H}_2\text{O} \right) \] and Thiourea (H\textsubscript{2}NCSNH\textsubscript{2}) were used as precursors for copper and sulphur source respectively. A green material starch acted as a capping agent and ammonia (aq.) as a complexing agent was used to adjust the pH values of the bath. Use of capping agents resulted in the growth of high quality nanoparticles as well as improved optoelectronics properties of the precursors. We choose starch as a capping material because it stabilizes the nanoparticles for many months against ambient atmosphere and also reduces the micro-strain of the product material. Ammonia (aq.) as a complexing agent is found to be useful in controlling the reaction in the synthesis process leading to stabilization of the nanoparticles well inside the capping material. Double de-ionized water was used as solvent for all the synthesis process. We had used 3% starch in de-ionized water to bring quantum confinement in CuS nanoparticles that makes the solution well dispersed and clear. The variation of starch in a small percentage range is expected to result in shape and size-oriented nanostructures. The quantum confinement below 3% starch is found to be ineffective and beyond 5%, the matrix solution appears to be bulky. Maintenance of volumetric ratio for the precursors at 1:2 resulted in improved grain structures as well as optoelectronics properties of the product materials. The synthesized nanoparticles (black precipitates) were then (after 24h or more) filtered. The precipitates were then washed several times using double de-ionized water. The washed precipitates were dried in a hot air oven at 80\degree C and after grinding well to powder form were used to characterize with X-ray diffraction (XRD). The filtrate solution was used for high resolution electron microscopy (HRTEM) and other optical characterizations. Similar procedures were adopted to synthesize starch capped and uncapped copper sulphide at the other molar concentration (0.1M–0.001M) and temperature (2\degree C–86\degree C) (S\textsubscript{2}–S\textsubscript{14}, S\textsubscript{16}–S\textsubscript{20}) keeping the other growth parameters constant. The synthesis mechanism is schematically illustrated in Figure 1.

2.2 Synthesis and characterization

Initially, 100 ml de-ionized water was taken in a glass vessel where 3% starch was dissolved at room temperature (~30\degree C). Now, the 3% starch mixed de-ionized water was poured in two separate glass vessels in the volumetric ratio 1:2 where copper acetate monohydrate (0.1M) and thiourea (0.1M) were dissolved. A magnetic stirrer was kept vigorously stirring to dissolve the solutes. Ammonia (aq.) was added drop wise to the starch capped copper ion (Cu\textsuperscript{++}) complex
to make the solution alkaline. Adjusting pH to 11, a clear and homogeneous solution was obtained. Adding Thiourea solution drop wise to this alkaline copper ion complex, the final copper sulphide matrix solution was obtained. The synthesized sample became golden brown in color and black precipitates were formed. The $\text{H}^+$ ions of ammonia (aq.) are found to be responsible for the color change. The synthesized sample was indexed as S1.

For structural and morphological study, the as synthesized product was characterized with X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) technique respectively. The precipitate in powder form was used to record the diffractograms with copper $K\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$) and $2\theta$ in the range $0^\circ$–$80^\circ$ and scanning rate $0.05^\circ$ operated at 40 kV 40 mA. HRTEM (JEM 2100) recorded the morphology as well as selected area electron diffraction (SAED) pattern along with prominently observed d-value of different crystallographic planes of the synthesized nanoparticles at an accelerating voltage 200 kV and beam current 102 $\mu$A. Optical absorption and emission spectra were measured in the wavelength range 300–800 nm and 300–700 nm (excitation wavelength 325 nm and 350 nm) using USB-2000 UV-visible and F-2500 Hitachi FL spectrometer respectively. Fourier transform infra-red (FTIR) spectra in the wave number range 4000–400 cm$^{-1}$ were recorded by an FTIR spectrometer (IR affinity-1, Shimadzu, Japan). The temperature dependence of electrical resistivity and conductivity of ionic colloidal copper sulphide solutions was determined using a standard conductivity cell. A conductivity cell in a measuring solution is placed in the inverting input path of an operational amplifier. When AC voltage of constant amplitude and suitable frequency is applied to the system then for a given feedback resistance the output is linearly proportional to the conductance of the solution. On multiplying conductance by cell constant gives the ionic conductivity of the solution.
3 Results and discussion

3.1 Structural and morphological investigation

Figure 2(a) shows the XRD patterns of the starch capped (S1, S2, S5) and uncapped (S8) copper sulphide nanoparticles synthesized at room temperature (\(\sim 30^\circ C\)) (S1, S5, S8) and at 85°C (S2) respectively and different molar concentrations as listed in Table 1. The diffraction peaks of both capped and uncapped synthesized copper sulphide powder contain mixed phases along with some weak diffraction peaks superimposed on starch matrix and de-ionized water. The diffraction pattern shows the most prominent peaks of (102), (103), (110) and (203) crystallographic planes corresponding to \(2\theta\) at 29.51°, 32.09°, 48.23° and 59.37° respectively which correspond to typical CuS (covellite) phase having hexagonal structure with few weak peaks of other phases of CuS such as djurleite(Cu\(_{1.96}\)S), anilite(Cu\(_{1.75}\)S) and chalcocite(Cu\(_2\)S) phases. XRD results also agree with the indexed lattice planes of selected area electron diffraction (SAED). The estimated lattice parameters (Table 1) match closely with standard data (ICSD: 061797) and also with literatures [21, 22]. The peaks of room temperature synthesized CuS of 0.1M solution are found to be highly intense and broad compared to the high temperature and low molar concentration synthesized CuS. Thus, we obtained mono-dispersed and crystalline nanosize CuS nanoparticles in sample S1 and S8. With increase of temperature to 85°C (S2) and lowering molar concentration (S2, S5), the peak positions shifted close to djurleite phase of CuS (ICSD: 100334). The diffraction patterns of samples S1 and S2 are very similar with difference in terms of reflection indices and peak intensity only. The shifting of peaks is found to increase with decreasing concentration and increasing temperature of the bath resulting possibly from lattice contraction that may arise from increased surface to volume ratio of the synthesized nanoparticles. The induced local strain is found to be reduced suggesting increase in crystalline quality of the product material. Thus, we observe phase transition from covellite to djurleite on increasing the growth temperature and lowering molar concentration. This phase transition is also supported by PL emission. The slight reduction in lattice constant value compared to its bulk value is found to be due to surface effects as reported by others [15].

Debye-Scherrer (D-S) method was used to estimate the average crystallite size of the synthesized nanoparticles employing the D-S equation

\[
\beta = \frac{k \lambda}{D \cos \theta} \quad \text{or} \quad \cos \theta = \left(\frac{k \lambda}{D \beta}\right) \frac{1}{2}
\]

with shape factor \(k \sim 0.9\), wavelength of CuK\(_\alpha\) radiation \(\lambda \sim 0.15406\) nm, crystallite size \(D\) and Bragg angle \(\theta\). The XRD spectra of as synthesized CuS nanostructures of samples S1, S2, S5 (capped) and S8 (uncapped) are shown in Figure 2. The diffraction patterns show the presence of various diffraction peaks corresponding to different crystallographic planes.

![Figure 2. (a) XRD spectra of as synthesized CuS nanostructures of samples S1, S2, S5 (capped) and S8 (uncapped).](image-url)
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Size $D$, full width at half maximum (FWHM) $\beta$ (in radians) of the most preferential peak and peak position $\theta$ for the corresponding $(hkl)$ planes [23]. A plot with $1/\beta$ along $x$-axis and $\cos \theta$ along $y$-axis gives a straight line. From the slope of the plot, the average grain size was calculated for the samples (plots not shown). Williamson-Hall (W-H) plot was used to find the average crystallite size and strain from induced broadening which arises from crystal defects and distortions [24, 25]. The W-H relation contains a tensile strain $\varepsilon$ in addition to $D$-S term as given by the equation

$$\beta \cos \theta = k \lambda \frac{D}{\varepsilon} + 4 \varepsilon \sin \theta \tag{2}$$

Figure 2. (b), (c) (S1, S2): Average particle size and Strain (W-H plot); (d), (e) (S1): Stress and energy density estimation (W-H plot) of CuS nanoparticles.

and S2 are very similar with difference in terms of reflection indices and peak intensity only. The shifting of peaks is found to increase with decreasing concentration and increasing temperature of the bath resulting possibly from lattice contraction that may arise from increased surface to volume ratio of the synthesized nanoparticles. The induced local strain is found to be reduced suggesting increase in crystalline quality of the product material. Thus, we observe phase transition from covellite to djurleite on increasing the growth temperature and lowering molar concentration. This phase transition is also supported by PL emission. The slight reduction in lattice constant value compared to its bulk value is found to be due to surface effects as reported by others [15]. Debye-Scherrer (D-S) method was used to estimate the average crystallite size of the synthesized nanoparticles employing the D-S equation

$$\beta = \frac{k \lambda}{D \cos \theta} \quad \text{or} \quad \cos \theta = \left( \frac{k \lambda}{D} \right) \frac{1}{\beta} \tag{1}$$

with shape factor $k \sim 0.9$, wavelength of CuKα radiation $\lambda \sim 0.15406$ nm, crystallite size $D$, full width at half maximum (FWHM) $\beta$ (in radians) of the most preferential peak and peak position $\theta$ for the corresponding $(hkl)$ planes [23]. A plot with $1/\beta$ along $x$-axis and $\cos \theta$ along $y$-axis gives a straight line.
From the slope of the plot, the average grain size was calculated for the samples (plots not shown). Williamson-Hall (W-H) plot was used to find the average crystallite size and strain from induced broadening which arises from crystal defects and distortions [24, 25]. The W-H relation contains a tensile strain $\varepsilon$ in addition to D-S term as given by the equation

$$
\beta \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta .
$$

A plot between $\sin \theta$ and $\beta \cos \theta$ along abscissa and ordinate respectively gives a straight line. The grain size $D$ was estimated from the $y$-intercept and the strain $\varepsilon$ from the slope of the plot respectively. The results of D-S and W-H plots also well match with HRTEM results. The particle size increases with increasing molar concentration of the solutions. This may be due to aggregation of large number of nuclei produced at faster rate in increased molar solution or slow rate of reaction amongst the constituents of the precursor [10, 15]. Using the general Hooke’s law of elasticity, $\sigma = \varepsilon Y$ and $u = \frac{1}{2} \varepsilon^2 Y$ equation (2) in terms of strain $\varepsilon$ and energy density $u$ can be expressed as

$$
\beta \cos \theta = \frac{k \lambda}{D} + \frac{4 \sigma \sin \theta}{Y} \quad \text{and} \quad \beta \cos \theta = \left( \frac{k \lambda}{D} \right) + 4 \sin \theta \left( \sqrt{\frac{2u}{Y}} \right) .
$$

The W-H plots of (3) & (4) in a similar manner give stress $\sigma$ and energy density $u$ of the synthesized nanocrystals respectively for the sample S1. Stress and energy density were also estimated for the other three samples. Young’s modulus $Y$ as estimated from stress-strain relation was found to be 98.98 GPa for the sample S1. Young’s modulus for different $(hkl)$ planes and lattice parameters $(a, c)$ for a hexagonal crystal structure in terms of elastic compliance $S_{ij}$ of CuS [26] is expressed as

$$
Y = \left[ h^2 + \frac{(h + 2k)^2}{3} + \left( \frac{a l}{c} \right)^2 \right]^2 \left[ S_{11} \left( h^2 + \frac{(h + 2k)^2}{3} \right)^2 + S_{33} \left( \frac{a l}{c} \right)^4 + (2S_{13} + S_{44}) \left[ h^2 + \frac{(h + 2k)^2}{3} + \left( \frac{a l}{c} \right)^2 \right] \right]^{-1} ,
$$

where the elastic compliances $S_{11}$, $S_{13}$, $S_{33}$ and $S_{44}$ have the values $12.6 \times 10^{-12}$ m$^2$/N, $-0.8 \times 10^{-12}$ m$^2$/N, $6.7 \times 10^{-12}$ m$^2$/N and $75.3 \times 10^{-12}$ m$^2$/N respectively. The dislocation density $\delta$ was also calculated using the relation $\delta = 15 \varepsilon/\left(aD\right)$. Estimated different micro-structural parameters have been listed in Table 1. It is observed, with reduction of molar concentration of the solutions, the tensile stress in the synthesized copper sulphide nanoparticles changes
Table 1. Micro-structural parameters of CuS nanocrystals: growth temperature ($T\, ^\circ C$); average grain size ($D$); dislocation density ($\delta$); micro-strain ($\varepsilon$); stress ($\sigma$); Young’s modulus ($Y$) and energy density ($u$)

<table>
<thead>
<tr>
<th>Sample/ Molarity/ Temp.</th>
<th>Lattice const. ($a/c$)</th>
<th>$D$ (nm)</th>
<th>$\delta \times 10^{-3}$ (1 in)/nm$^2$</th>
<th>$\varepsilon \times 10^{-3}$</th>
<th>$\sigma$ (MPa)</th>
<th>$Y$ (GPa)</th>
<th>$u$ (J/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1/0.1M/30$^\circ$C</td>
<td>3.77/16.03</td>
<td>10/9</td>
<td>28.25</td>
<td>6.39</td>
<td>632.5</td>
<td>98.98</td>
<td>2.78</td>
</tr>
<tr>
<td>S8/0.1M/30$^\circ$C</td>
<td>3.77/16</td>
<td>13/11</td>
<td>19.6</td>
<td>5.91</td>
<td>241</td>
<td>29.85</td>
<td>10.93 x 10$^{-4}$</td>
</tr>
<tr>
<td>S5/0.005M/30$^\circ$C</td>
<td>3.76/16.17</td>
<td>7/3</td>
<td>632.9</td>
<td>-47.6</td>
<td>-882.5</td>
<td>18.54</td>
<td>12.27</td>
</tr>
<tr>
<td>S2/0.04M/85$^\circ$C</td>
<td>3.73/16.12</td>
<td>9/8</td>
<td>307.89</td>
<td>-61.25</td>
<td>-2.48</td>
<td>0.04</td>
<td>7.5 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

To compressive stress. Further, the compressive stress reduced significantly with increase of molar concentration and temperature. This effect of molar concentration and temperature also indicates the phase transition of covellite to djurleite phase of CuS. The energy density value of the product for the capped material is also very large compared to that of the uncapped material which signifies strong quantum confinement in the capped material. This is also evident from PL emission.

Figure 3(a) shows HRTEM morphology with uniform and homogeneous distribution of spindle type CuS nanoparticles which are actually the agglomerates of nanoparticles of size 3–13 nm (Figure 3(b) & (d)) embedded in starch matrix. The SAED pattern (Figure 3(c)) for the typical CuS synthesized by keeping volumetric ratio Cu:S = 1:2 and molarity 0.005M (S5) exhibits some concentric broad rings with a central halo and bright spots. The broadness is possibly originated from the quantum confinement of nanoparticles embedded in starch matrix [27]. The concentric rings of the SAED pattern are found to arise from hexagonal crystal structure of CuS. The corresponding crystal planes may be indexed to (102), (103), (008), (108) and (211).

The nanosize particle distribution as revealed by HRTEM morphology clearly shows the well confinement of spindle particles in starch matrix. The rings are broad with bright spots which suggest that the synthesized nanoparticles possess good crystalline quality. Figure 3(e) (Inset) also shows the $d$-value of 0.29 nm in spindle particles corresponding to (102) plane. This indicates the prominent growth direction along (102) atomic plane. There is a little deviation in particle size measurement from HRTEM compared to XRD measurement. This is because in HRTEM measurements the grain size may be controlled by some defects induced in the nanocrystal or grains may contain several coherently diffracting domains in the crystal [28].
The UV-vis. absorption studies show good blue shift of sharp absorption edge for all the synthesized samples (Table 2). The strong blue shift in the visible region may be attributed to quantum confinement of the nanoparticles in the matrix material which results in an enhancement of band gap to 2.8–3.85 eV on lowering molar concentration compared to its bulk. Starch is expected to play a key role in bringing the quantum confinement in the samples through its prime ligand -OH group. The sharp absorption edge near the band edge indicates formation of good quality CuS nanoparticles with good crystalline quality and low defect density of the synthesized material. Fig.4 shows the typical absorption spectra of CuS nanostructures synthesized at different molar concentrations and temperatures. The observed band gaps were estimated from \((\alpha h\nu)^2 \text{ vs. } h\nu\) plots (Tauc-plot) extrapolating the linear part of the plot to zero absorption coefficient \((\alpha)\) value on \(h\nu\) axis. The plots are found to be linear which indicates that the mode of transition is of direct nature [29]. The observed blue shift for the uncapped CuS is found to be least compared to the capped CuS signifying the effect of starch in enhancement of quantum confinement.

Figure 4(e) exhibits an increase of band gap with lowering molarities which is in
Table 2. Optical parameters of CuS/Starch: molarity (M); growth temperature (T); excitation wavelength (λe); near band gap emission (λne); impurity emission (λi); average absorption edge (λa); band gap (Eg) from Tauc plots; blue shift (ΔE) and Stock shift (λs) well agreement with others [11]. The particle size also increases with molarities (Figure 4(f)). This may be due to faster rate of reaction between constituent ions of the precursors in high molar solution resulting in further growth of CuS nanoparticles and their subsequent aggregation. Fig.4 (g) shows temperature dependence of band gap signifying strong quantum confinement effect of the as prepared nanoparticles.

PL spectra of the copper sulphides show near UV emissions around 362 nm to 395 nm measured at excitation wavelength 325 nm and weak extrinsic emission around 460 nm to 492 nm (Figure 5 S1, S5, S7). The near band gap emissions (NBE) and the impurity emissions for the samples measured at excitation wavelength 350nm are listed as shown in Table 2. The PL peaks become more intense with decreasing molar concentration of the solutions (Figure 5(b) S3, S4, S6, S11 and S12). The peak intensity also increases with decreasing growth temperature for the same molar solutions (Figure 5(a,b) S9, S10; S3, S11, S12; S2, S13 and S6, S14). The PL peaks of the uncapped CuS are sharp and exhibit the same nature of NBE and impurity emission except having difference in terms of emission intensity. (Figure 5(c), inset). The low temperature synthesized CuS nanoparticles exhibit enhancement of band gap emission intensity and on increasing growth temperature, the intensity noticeably decreases which may be due to the possible phase change from covellite to djurleite phase of CuS. The reduction in luminescence with growth temperature is expected to occur owing to removal of intrinsic impurities and surface defects.

<table>
<thead>
<tr>
<th>Sample/ Molarity/ T °C</th>
<th>λe (nm)</th>
<th>λne (nm)</th>
<th>λi (nm)</th>
<th>λa (nm)</th>
<th>EG (eV)</th>
<th>ΔE (b(eV))</th>
<th>λs (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/0.1M/30°C</td>
<td>325</td>
<td>389</td>
<td>492</td>
<td>392</td>
<td>3.19</td>
<td>0.69</td>
<td>3</td>
</tr>
<tr>
<td>S10/0.1M/2°C</td>
<td>350</td>
<td>410</td>
<td>496</td>
<td>432</td>
<td>3.02</td>
<td>0.52</td>
<td>22</td>
</tr>
<tr>
<td>S9/0.1M/85°C</td>
<td>350</td>
<td>471</td>
<td>495</td>
<td>398</td>
<td>3.18</td>
<td>0.68</td>
<td>73</td>
</tr>
<tr>
<td>S2/0.04M/85°C</td>
<td>350</td>
<td>467</td>
<td>492</td>
<td>402</td>
<td>3.27</td>
<td>0.77</td>
<td>65</td>
</tr>
<tr>
<td>S13/0.04M/8°C</td>
<td>350</td>
<td>468</td>
<td>495</td>
<td>375</td>
<td>3.32</td>
<td>0.82</td>
<td>93</td>
</tr>
<tr>
<td>S3/0.01M/14°C</td>
<td>350</td>
<td>450</td>
<td>495</td>
<td>455</td>
<td>3.35</td>
<td>0.75</td>
<td>5</td>
</tr>
<tr>
<td>S11/0.01M/32°C</td>
<td>350</td>
<td>467</td>
<td>495</td>
<td>388</td>
<td>3.32</td>
<td>0.82</td>
<td>79</td>
</tr>
<tr>
<td>S12/0.01M/85°C</td>
<td>350</td>
<td>452</td>
<td>495</td>
<td>381</td>
<td>3.31</td>
<td>0.81</td>
<td>71</td>
</tr>
<tr>
<td>S5/0.005M/30°C</td>
<td>325</td>
<td>395</td>
<td>460</td>
<td>373</td>
<td>3.34</td>
<td>0.84</td>
<td>22</td>
</tr>
<tr>
<td>S4/0.001M/85°C</td>
<td>350</td>
<td>445</td>
<td>494</td>
<td>340</td>
<td>3.66</td>
<td>1.16</td>
<td>105</td>
</tr>
<tr>
<td>S7/0.05M/30°C</td>
<td>325</td>
<td>362</td>
<td>485</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S6/0.07M/5°C</td>
<td>350</td>
<td>450</td>
<td>496</td>
<td>331</td>
<td>3.85</td>
<td>1.35</td>
<td>119</td>
</tr>
<tr>
<td>S14/0.07M/85°C</td>
<td>350</td>
<td>458</td>
<td>496</td>
<td>490</td>
<td>3.22</td>
<td>0.72</td>
<td>32</td>
</tr>
<tr>
<td>S8/0.1M/30°C</td>
<td>350</td>
<td>398</td>
<td>501</td>
<td>446</td>
<td>2.80</td>
<td>0.30</td>
<td>48</td>
</tr>
</tbody>
</table>
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Figure 4. (a), (c) UV-Vis. of samples S1, S2, S3, S4 & S5; (b), (d) Corresponding Tauc-plot of Samples S1 & S4 (inset), (e) Mol.-Band gap plot of samples at temperature 85°C; (f) Mol.-Crystallite size plot (Inset); (g) Temperature-Band Gap plot of samples of molarity 0.01M.

Figure 5. (a) PL plots of samples S2 (0.04M), S9 (0.1M), S10 (0.1M), S13 (0.04M) & S14 (0.07M); (b) S3 (0.01M), S4 (0.001M), S6 (0.07M) & S11; (c) S8 (0.1M).
Most of the PL spectra are observed to be broad. So, band edge emission and green bands are not distinguishable. Actually, the spectra contain some overlapping bands or intra-band spectra. An attempt was made to conduct deconvolution of few PL spectra into Gaussian/Lorentz shaped components (Figure 5(d-h)). The deconvoluted PL spectra of the sample S1 exhibited one dominant peak at 387 nm and three shoulder peaks positioned at 412 nm, 445 nm and 487 nm (Figure 5(d)). These intra-band peaks are not likely to originate from fine structure of the excitonic emission; instead they are expected to originate from several defect states that exist in the synthesized nano-crystal as reported by others [30]. The deconvoluted peaks of few PL spectra have been listed in Table 3. The energy states for bulk CuS and different surface state emissions for the synthesized CuS nanostructures have been tentatively illustrated in Figure 5(i) and (j) respec-
Table 3. List of deconvoluted peaks for the PL spectra obtained with different excitation wavelengths ($\lambda_e$).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Analysis of deconvoluted PL peaks (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_e = 325$ nm</td>
</tr>
<tr>
<td>S1</td>
<td>387 — 412 — 445 — 487</td>
</tr>
<tr>
<td>S3</td>
<td>— — — —</td>
</tr>
<tr>
<td>S5</td>
<td>379, 375 — 415 — 459</td>
</tr>
<tr>
<td>S6</td>
<td>— — —</td>
</tr>
<tr>
<td>S7</td>
<td>367, 370 — 392 — 427</td>
</tr>
</tbody>
</table>

Effectively, the UV-Blue emission band may be attributed to different surface states of the nanoparticles while the near green band to defective CuS/Starch interface oxidation states of copper ions lying below the conduction band \[17, 28, 31\]. The observed NBE is attributed to surface induced trapped luminescence along with band to band recombination whereas the impurity emission is related to native defects owing to dangling bonds of copper sulphide nanocrystallite. This is also evident from the as calculated high value of Stoke’s shift (Table 2). The sharp emission peaks can be attributed to the quantum confined enhanced band gap emissions which become strong on lowering molar concentration. Strong band gap emission signifies good crystalline quality and aspect ratio of the as-synthesized spindle particles \[32\]. The NBE red shifted on lowering molarities and on increasing growth temperature which may be due to increased defects or increased strain induced in the nanocrystal. The PL distribution around the UV-Blue region is attributed to uniform distribution of well defined spindle particles \[33\]. The low molar synthesized CuS nanocrystal may be exploited in fabrication of UV-BlueLED.

Figure 5. (i) Tentative energy level diagram for bulk CuS, (j) Nanosize CuS (S10).

Figure 6. FTIR spectra of pure (S15) and starch capped nanoparticles (S1).
3.3 FTIR analysis

FTIR spectra of different vibration modes of pure starch (ST) and starch capped CuS (CuS/ST) located at different regions are shown in Figure 6. The absorption peak of -OH group of starch of CuS/ST located at 3435 cm$^{-1}$ is slightly shifted from that of ST located at 3419 cm$^{-1}$ which indicates a strong interaction between CuS nanoparticles and -OH group of starch. Thus CuS nanoparticles and -OH group of starch may be bound by chemical interaction which prevents CuS nanoparticles from aggregation in the nanocrystals [34]. The absorption band at 615 cm$^{-1}$ is attributed to Cu-S vibration band of CuS nanoparticles which matches well with results of others [35]. The peak located around 1604 cm$^{-1}$ is attributed to C=O stretching mode while strong peak around 1014 cm$^{-1}$ may be due to the -C-O group of starch indicating CuS nanoparticles are well confined in starch matrix.

![Figure 6. FTIR spectra of pure (S15) and starch capped nanoparticles (S1).](image)

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Absorption region (cm$^{-1}$)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-S stretching</td>
<td>400–650</td>
<td>small &amp; weak</td>
</tr>
<tr>
<td>C=O stretching</td>
<td>1604</td>
<td>medium</td>
</tr>
<tr>
<td>-C-O stretching</td>
<td>1014</td>
<td>medium &amp; broad</td>
</tr>
<tr>
<td>O-H stretching</td>
<td>3435</td>
<td>Medium &amp; broad</td>
</tr>
</tbody>
</table>

4 Ionic Conductivity Study

The report on ionic conductivity studies on an electrolytic ionic solution like CuS is limited in literature. Hence an attempt has been made to find the ionic char-
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acteristics of present synthesized CuS nanoparticles. In an ionic solution, the electrical conductivity is entirely due to motion of ions. Copper vacancies in the synthesized material are expected owing to thiourea which is a source of sulphur ions. As one mechanism of ionic contribution towards electrical conductivity, it may be presumed that as one Cu and one S atom become mobile as \( \text{Cu}^{++} \) and \( \text{S}^{-} \) ions in the solution, a \( \text{Cu}^{++} \) vacancy (2 electrons) and a \( \text{S}^{-} \) vacancy (2 holes) are created. As a result of interaction of these two types of vacancies, electrons are excited leading to electrical conductivity of the material [6].

The electrical conductivity variation of ionic CuS solution with temperature in temperature range 286–358 K (S19) and 278–359 K (S17) was measured using a standard conductivity cell. From the measured conductivity, the resistivity of the ionic solution at different temperatures was determined. Resistivity vs. inverse temperature plot is found to exhibit the semiconducting nature of the synthesized materials. The results are also close to others [36, 37] (Figure 7(a) & (b)). The ionic conductivity is expressed by the exponential relation (Arrhenius equation)

\[
\sigma_i = \sigma_{i0} \exp(-E_a/k_B T) \quad \text{or resistivity} \quad \rho_i = \rho_{i0} \exp(E_a/k_B T)
\]

with pre-exponential factors \( \sigma_{i0} \) and \( \rho_{i0} \), activation energy \( E_a \) for the conduction process of ions in the solution and absolute temperature \( T \) of ionic solution [18]. The slope of the resistivity vs. inverse temperature plot gives the activation energy which is calculated from the relation

\[
E_a = 2.303 \times k_B \times \text{slope} \quad \text{(eV)}
\]

where \( k_B = \) Boltzmann’s constant = 8.617 \times 10^{-5} \text{ eV/K}.

Table 5. Electrical properties of ionic CuS solution: growth temperature (\(^\circ\)C); ionic conductivity (\( \sigma \)); activation energy (\( E_a \)), molar conductivity (\( \Lambda \)); degree of dissociation (\( \alpha \)); ionic mobility (\( \mu \)); and diffusion coefficient (\( D \))

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molarity</th>
<th>Temperature</th>
<th>( \sigma \times 10^{-4} \Omega^{-1} \text{cm}^{-1} )</th>
<th>( \rho \Omega \text{cm} )</th>
<th>( E_a \text{ eV} )</th>
<th>( \Lambda \text{ cm}^2/(\Omega \text{mol}) )</th>
<th>( \alpha )</th>
<th>( \mu \times 10^{-4} \text{ cm}^2/(\text{sV}) \text{cm}^2/\text{s} )</th>
<th>( D \text{ cm}^2/\text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S16</td>
<td>0.1M</td>
<td>30</td>
<td>82.00</td>
<td>121.95</td>
<td>0.1248</td>
<td>82.00</td>
<td>0.753</td>
<td>11.29</td>
<td>4.60</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>41.56</td>
<td>240.59</td>
<td>85.0</td>
<td>0.791</td>
<td>11.13</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S17</td>
<td>0.07M</td>
<td>30</td>
<td>61.03</td>
<td>163.84</td>
<td>0.1383</td>
<td>87.19</td>
<td>0.794</td>
<td>11.37</td>
<td>6.79</td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>100.8</td>
<td>99.20</td>
<td>144.01</td>
<td>0.846</td>
<td>17.64</td>
<td>127.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S18</td>
<td>0.04M</td>
<td>30</td>
<td>38.00</td>
<td>263.16</td>
<td>0.1602</td>
<td>95.00</td>
<td>0.845</td>
<td>11.62</td>
<td>12.88</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>12.32</td>
<td>811.86</td>
<td>123.17</td>
<td>0.932</td>
<td>13.70</td>
<td>51.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S19</td>
<td>0.01M</td>
<td>30</td>
<td>12.98</td>
<td>770.41</td>
<td>0.1325</td>
<td>129.8</td>
<td>0.934</td>
<td>14.40</td>
<td>66.43</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>38.11</td>
<td>262.38</td>
<td>381.11</td>
<td>0.962</td>
<td>41.06</td>
<td>250.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S20</td>
<td>0.001M</td>
<td>30</td>
<td>12.48</td>
<td>801.09</td>
<td>0.1007</td>
<td>1248</td>
<td>0.991</td>
<td>130.47</td>
<td>265.61</td>
</tr>
</tbody>
</table>

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Table 5 shows the effect of temperature and concentration on various ionic parameters. Different ionic parameters such as molar conductivity ($\Lambda$), degree of dissociation ($\alpha$), ionic mobility ($\mu$) and diffusion coefficient ($D$) of the ionic CuS solutions (S16–S20) were estimated from conductivity data of the samples (Table 5). The table shows the decrease of resistivity with increase of growth temperature exhibiting semiconducting nature of the as synthesized CuS samples. The resistivity is also observed to be decreased considerably with increase of concentration of the precursors which may be due to creation of excess copper vacancies giving rise to a large number of free holes [20]. The degree of ionization and the molar conductivity increase with increasing dilution of the ionic solutions which is in well agreement with the Debye-Huckel theory for electrolytes. The activation energy-molarity plots in the molar concentration range 0.001M–0.1M are shown in Figure 7(c). The plots are found to match well with those of an ionic solution. The activation energies for the mobile ions are also in good agreement with others [36]. Table 5 shows decrease of activation energy with concentration of the precursors. The molar concentration–molar conductivity plots of ionic CuS solution exhibits weak electrolytic nature of CuS (Figure 7(d)). Debye-Huckel-Onsager relation was used to determine the degree of dissociation of the ionic CuS solution from the experimentally measured values.

![Figure 7. (a), (b) Resistivity vs. inverse temperature plots for ionic CuS solutions of samples S19 & S17; (c) Molarity vs. activation energy curve for ionic CuS solution; (d) Variation of molar conductivity with concentration.](image-url)
of molar conductance and the estimated values of molar conductance at infinite dilution [39, 40]. The estimated values of degree of dissociation for all the samples are also found to demonstrate characteristic behavior of weak electrolytes. The mobility reduces at higher concentrations which may be due to inter-ionic effect. The ionic mobility and the diffusion coefficients of CuS ionic solutions are also found to be close to the reported works [18, 38, 40]. Thus CuS can transport charge via both ions and electrons and hence the same may be one of the potential candidate to be used as mixed ionic electronic conductors (MIECs) for the development of electrochemical technology [19].

5 Conclusion

A spindle type particle distribution was obtained from the structural morphology of CuS nanoparticles synthesized through chemical route. The starch as capping agent was found to be useful in controlling the structural morphologies as well as in confinement of nanoparticles. Adjusting the pH value of the solution the release of S$^{2-}$ ions from Thio can be controlled. The XRD measurement showed covellite phase of CuS superimposed on the matrix materials. A phase transition from covellite to djurleite on increasing the growth temperature and lowering molar concentration has been observed. The lattice constants have a slight deviation from bulk suggesting the developments of strain and stress along with others structural defects. The micro-structural parameters have been estimated and correlated with growth parameters. A reduction of molar concentration of the solutions may change the tensile stress to compressive stress in the synthesized copper sulphide nanoparticles. HRTEM morphology exhibits well defined spindle type nanoparticles having average size 3–13 nm. It is observed from the images that the spindle particles seem to be as a result of diffusion induced agglomeration of some individual spherical particles of average diameter 13nm. The optical properties of the CuS nanoparticles exhibited good blue shift of absorption edge with enhancement of band gap from 2.8 eV to 3.85 eV with lowering of molar concentrations and growth temperatures. The PL spectra show a non-symmetric emission around 362–492 nm. This UV-Blue emission corresponds to the spindle particle distribution and hence the intensity increases because of their good aspect ratio synthesized at low molar concentration. The reduction in luminescence with growth temperature may be owing to removal of intrinsic impurities and surface defects. FTIR spectra show absorption peak of -OH group of starch of CuS/ST located at 3435 cm$^{-1}$ which is slightly shifted from that of starch located at 3419 cm$^{-1}$ indicating a strong interaction between CuS nanoparticles and -OH group of starch. The absorption band at 615 cm$^{-1}$ is attributed to Cu-S vibration band of CuS nanoparticles which matches well with results of others. The temperature vs. resistivity plot confirms semiconducting nature of the synthesized CuS nanoparticles. The activation energy in the range 0.10 -0.16 eV exhibits the characteristic behavior of an ionic solution. The ionic
parameters were correlated with growth conditions. The estimated ionic parameters suggest a weak electrolytic nature of ionic CuS solution. The synthesized material may be explored for an optoelectronic device such as UV-Blue LED. Since CuS/starch can transport charge as ions and electrons, it may also be considered as one of the prime mixed ionic electronic conductors (MIECs) for the development of electrochemical technology.

Acknowledgments

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References

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