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Cite this: New J. Chem., 2013, 37, 1470

Received (in Montpellier, France) 17th December 2012, Accepted 17th February 2013

DOI: 10.1039/c3nj41142g

www.rsc.org/njc

1. Introduction

Chalcogenides are an important class of materials that have found potential uses in catalysis, energy storage and conversion, and optoelectronic devices.^{1–5} Copper sulfide (Cu_xS) is one of the chalcogenides that has received considerable attention in recent years owing to its wide stoichiometric composition [*i.e.*, Cu₂S, Cu_{1.96}S, Cu_{1.94}S, Cu_{1.8}S, Cu_{1.75}S, and CuS], diverse morphology, and non-linear optical property. In particular, the bandgap of Cu_xS can be varied in a wider range (1.2 to 2.5 eV) with stoichiometric composition (x = 1-2),⁶ making it a highly desirable material for solar cells,^{7–9} nonvolatile memory devices,^{10,11} and gas sensing¹² applications. Furthermore, Cu_xS is a potentially interesting material for cold cathodes,¹³ and lithium ion batteries.¹⁴

The synthesis technique and parameters involved play a crucial role in controlling the morphology and stoichiometry of Cu_xS, which determines their structural, optical, and electrical properties. Low-temperature solution-based techniques, such as sonochemical,¹⁵ sol-gel,¹⁶ hydrothermal,¹⁷ solvothermal,¹⁸ microemulsion,¹⁹ and electrodepostion,^{20,21} are commonly

Influence of precursor concentration, surfactant and temperature on the hydrothermal synthesis of CuS: structural, thermal and optical properties

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Herein we demonstrate the synthesis and formation mechanism of copper sulfide (CuS and Cu₂S) by a simple hydrothermal process in the temperature range of 150–250 °C. The molar concentration ratio of copper nitrate to sodium thiosulfate precursor, and the reaction temperature play important roles in determining the morphology and composition of the product. At a higher thiosulfate concentration, elemental sulfur precipitates out along with CuS. However, the elemental sulfur is degraded with increasing of the reaction temperature. The morphology of the as-synthesized product is primarily a sphere-like agglomeration of either nanoparticles and/or nanoplates. The surfactant is found to be indispensable for obtaining dispersed nanocrystals. The stability of CuS and the formation of different copper compounds at higher temperature are studied in detail using thermal analysis and X-ray diffraction (XRD). The phase pure CuS is found to be completely converted to CuO upon calcining in air at 800 °C. However, the *in situ* high temperature XRD measurements in a vacuum show complete conversion of CuS to Cu₂S at 600 °C without any intermediate phases. The optical bandgap of the as-synthesized CuS nanocrystals is measured to be ~ 1.7 eV.

employed to synthesize a wide variety of copper sulfide nanostructures, including nanoparticles,^{19,22} nanotubes,²³ nanowires,¹⁷ nanorods,²⁴ nanoplates,²⁵ and hollow spheres.^{26,27} These synthetic processes generally involve reagents such as Triton-X 100,¹⁹ dodecanethiol,²⁸ ammonium *O*,*O'*-dialkyldithiophosphates,²⁹ 1-butyl-3-methylimidazolium tetrafluoroborate,²⁶ 1-decanethiol,³⁰ and 1,2-hexadecanediol.³⁰ In the present study, we demonstrate the synthesis of CuS using very common and inexpensive reagents, such as copper nitrate and sodium thiosulfate, by a hydrothermal technique in a short reaction duration of 8 h.

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Previously, sodium thiosulfate has been used as a sulfur source to synthesize CuS nanocrystals²² and Cu₂S hexagonal dendrites³¹ using ethylene glycol and ammonia solution, respectively. This suggests that the reaction medium plays a significant role in controlling the shape, size and phase of the products. Here we demonstrate the synthesis of CuS clusters consisting of either nanoparticles and/or nanoplates by varying the molar ratio of copper nitrate to sodium thiosulfate precursors in an aqueous medium. Upon adding the surfactant to the reaction medium, dispersed nanoparticles or nanoplates are obtained. The formation mechanism of CuS and other products upon calcining the pristine CuS in air or under vacuum are discussed in detail using thermal analysis and high temperature *in situ* X-ray diffraction (XRD).

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2. Experimental details

2.1. Chemicals

Copper nitrate $[Cu(NO_3)_2 \cdot 3H_2O]$ and sodium thiosulfate $[Na_2S_2O_3 \cdot 5H_2O]$ (Merck, India), cetyl trimethylammonium bromide (CTAB, SRL, India), and ethanol (Changshu Yangyuan Chemical, China) were all of analytical grade and used without further purification.

2.2. Synthesis

241 mg of copper nitrate [1 mmol] and 496 mg of sodium thiosulfate [2 mmol] were mixed in 20 mL distilled water and stirred for 30 min [final concentration of Cu²⁺ and S₂O₃²⁻ were 0.05 M and 0.1 M respectively]. A yellow colored solution was obtained after 30 min of stirring. It was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated at 150, 180, and 250 °C for 8 h in a muffle furnace and then cooled under ambient conditions. The resulting greenish solution was placed in a centrifuge to separate the powder product from the solvent. The as-synthesized product was washed with water and ethanol sequentially several times and then dried at 60 $^\circ C$ for 4 h. Similar reactions were performed by varying the $Cu(NO_3)_2$: Na₂S₂O₃ molar concentration ratio (1:4 and 1:6) at 150, 180 and 250 $^\circ$ C for 8 h. The effect of the surfactant was studied by carrying out the reaction in the presence of CTAB with a molar concentration ratio of $Cu(NO_3)_2$: $Na_2S_2O_3 = 1:2$ at 150, 180 and 250 °C for 8 h.

2.3. Characterization

The morphology of the as-prepared product was examined with a Carl-ZEISS SUPRA 40 field emission scanning electron microscope (FE-SEM) and EVO 60 Carl-ZEISS SEM attached with an Oxford EDS detector. A transmission electron microscopy (TEM) study was performed with a FEI TECHNI-G² instrument operated at 200 kV. The crystal structure of the product was measured using XRD with a Rigaku Ultima-III in the 2θ range of 10–70° at a scan rate of 1° min⁻¹ with copper as the target. High temperature in situ XRD was carried out with a PANalytical X'pert pro instrument under vacuum with cobalt as the target. The thermal analysis was performed with a TG instrument (NETZSCH, Model: TG 209 F1) in presence of an air flow $(100 \text{ mL min}^{-1})$ with a heating rate of 10 °C min⁻¹. The optical property was measured by dispersing the as-synthesized CuS nanoparticles in ethanol and collecting the transmittance as a function of wavelength using a PerkinElmer Lambda 750 UV-vis spectrophotometer.

3. Results and discussion

3.1. Morphology

The morphology of the CuS products prepared at different temperatures, and with a varied concentration ratio of copper nitrate to sodium thiosulfate precursor, was characterized by FE-SEM and presented in Fig. 1. Fig. 1(a)–(c) show the FE-SEM images of the products obtained at 150, 180 and 250 °C, respectively, in 8 h with a [Cu(NO₃)₂:Na₂S₂O₃] = 1:2 molar ratio.



Fig. 1 FE-SEM images of the CuS product prepared at (a) 150 °C, (b) 180 °C, and (c) 250 °C in 8 h using the hydrothermal technique with a precursor molar ratio $[Cu(NO_3)_2 : Na_2S_2O_3] = 1 : 2$. Inset of (a)–(c) represent the magnified image of the corresponding sample. (d) FE-SEM image of the CuS product prepared at 150 °C in 8 h with a precursor molar ratio $[Cu(NO_3)_2 : Na_2S_2O_3] = 1 : 6$.

In the above cases, the morphology of CuS product is found to be near spherical with agglomerated nanoparticles and/or nanoplates. The FE-SEM image of the product obtained at 150 °C [Fig. 1(a)] shows a sphere-like morphology with a diameter in the range of 0.6 to 1.2 µm. The magnified image [inset, Fig. 1(a)] of these sphere-like structures shows that they appear to be constituted of particles of less than 100 nm in diameter. At a higher synthesis temperature (180 °C), the CuS product appears as clusters with sizes in the range of 0.5–1.0 µm [Fig. 1(b)]. These solid and compact clusters are found to be made of both the nanoparticles and nanoplates, as confirmed from the magnified image [inset, Fig. 1(b)]. The energy dispersive X-ray (EDX) spectrum of this sample [Fig. 1(b)] shows a 1:1 Cu:S atomic ratio, indicating the CuS phase, as shown in Fig. 2(a). Further increasing the synthesis temperature to 250 °C, achieved similar CuS clusters, with diameters in the range of 0.5-1.0 µm [Fig. 1(c)]. These clusters consist of nanoplates in the size range of 200-500 nm (length and width) with a thickness of 50–80 nm [inset, Fig. 1(c)]. From the morphology analysis, the CuS sphere-like products are found to be less compact and the formation of nanoplates predominates over the nanoparticles upon increasing the synthesis temperature from 150 °C [Fig. 1(a)] to 250 °C [Fig. 1(c)]. In the synthesis of CuS, the ratio of Cu to S precursor is expected to play a significant role. Therefore, we varied the thiosulfate concentration to study its effect on the resulting product. The morphology of the products obtained with molar concentration ratios of $[Cu(NO_3)_2:Na_2S_2O_3] = 1:4$ and $[Cu(NO_3)_2:Na_2S_2O_3] = 1:6$ at 150, 180 and 250 °C was characterized by FE-SEM. In all these six cases, similar clustered morphology was observed (not shown). However, the size of the clusters obtained with 1:4 and 1:6 molar ratio was found to be larger (*i.e.*, $1.0-2.0 \mu m$) than that obtained with a molar ratio of 1:2. These clusters were also found to consist of nanoparticles and nanoplates with sizes of 200-400 nm. Fig. 1(d)

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Fig. 2 EDX spectra along with Cu and S at% of samples prepared using (a) $[Cu(NO_3)_2 : Na_2S_2O_3] = 1 : 2 \text{ molar ratio at } 180 \degree C \text{ in } 8 \text{ h, and (b)} [Cu(NO_3)_2 : Na_2S_2O_3] = 1 : 6 \text{ molar ratio at } 150 \degree C \text{ in } 8 \text{ h.}$

shows a typical FE-SEM image of the CuS product obtained with a $[Cu(NO_3)_2: Na_2S_2O_3] = 1:6$ molar ratio at 150 °C, which has a similar compactness of the nanoparticles as obtained at 150 °C with a $[Cu(NO_3)_2:Na_2S_2O_3] = 1:2$ molar ratio [inset, Fig. 1(a)]. The EDX spectrum from the sample prepared with a [Cu(NO₃)₂:Na₂S₂O₃] molar ratio of 1:6 at 150 °C shows Cu (at% 19) and S (at% 81) without any other impurity [Fig. 2(b)]. The high S content is due to the large initial concentration of sodium thiosulfate taken for the synthesis. In previous work, mainly hollow sphere of CuS have been obtained. These hollow spheres were large in diameter (5-20 µm) and were prepared at a temperature higher than 120 °C in 1 to 2 days.^{26,27} Wang et al. synthesized CuS hollow spheres of diameter ~ 500 nm using CTAB as a surfactant in 23 h.³² Chen et al. reported the formation of CuS hollow spheres (diameter 6 μ m) at 180 $^{\circ}$ C in 24 h, whereas below 180 °C they obtained solid spheres.³³ In all of the above cases, the spheres were made of micro/nano flakes. Zhang et al. prepared CuS hollow spheres of diameters smaller than 100 nm using a Cu₂O spherical nanotemplate.³⁴ Unlike the previous work, we prepared sphere-like CuS clusters of much smaller sizes consisting of nanoparticles and/or nanoplates in a shorter duration of 8 h and these products are highly reproducible from experiment to experiment.

3.2 Effect of surfactant

Use of a surfactant is known to significantly affect the agglomeration of particles. As the CuS product was found to be clusters consisting of nanoparticles and/or nanoplates, a surfactant was employed to reduce the agglomeration. CuS was synthesized at 150, 180 and 250 °C in the presence of 182 mg (0.5 mmol) CTAB surfactant while maintaining the molar ratio of the precursors $[Cu(NO_3)_2: Na_2S_2O_3 = 1:2]$ and reaction time (8 h). As expected, the resulting product was found to be not agglomerated. Fig. 3(a) and (b) show the FE-SEM and TEM images of distinct CuS nanoparticles obtained at 150 °C in the presence of CTAB, respectively. These nanoparticles appear to be elongated with size in the range 40-100 nm. Fig. 3(c) shows the corresponding high-resolution TEM (HRTEM) image of a CuS nanoparticle. The measured lattice spacing of 2.745 Å is matched to the spacing between the (006) planes of CuS [JCPDS card no. 00-006-0464]. Fig. 3(d) and (e) represent the FE-SEM and TEM images of the product obtained at 180 °C in 8 h, respectively. In this case, hexagonal nanoplates are found along with the elongated nanoparticles [Fig. 3(e)]. The size of these elongated nanoparticles



Fig. 3 FE-SEM (left) & TEM (middle) images of the CuS samples prepared at (a, b) 150 °C (d, e) 180 °C, and (g, h) 250 °C, in 8 h using the hydrothermal technique in presence of CTAB with $[Cu(NO_3)_2 : Na_2S_2O_3] = 1 : 2$. HRTEM (right) images of the nanoparticles/nanoplates prepared at (c) 150 °C, (f) 180 °C, and (i) 250 °C. Inset of (c), (f) and (i) represent SAED pattern of corresponding samples.

and hexagonal plates are measured to be in the range of 40 to 100 nm. Fig. 3(f) shows the HRTEM image of the nanoparticles obtained at 180 °C. The measured lattice spacing of 2.805 Å is matched to the spacing between the (103) planes of CuS [JCPDS card no. 00-006-0464]. Further increasing the hydrothermal synthesis temperature to 250 °C, the product morphology is found to be nearly same [Fig. 3(g)] as that obtained at 180 °C. However, the TEM image [Fig. 3(h)] clearly shows primarily hexagonal nanoplates in the size range of 40-100 nm along with a few elongated particles. Fig. 3(i) displays the HRTEM image of a nanoplate obtained at 250 °C. Here the measured lattice spacing of 2.996 Å is matched to the spacing between the (102) planes of CuS [JCPDS card no. 00-006-0464]. Inset of Fig. 3(c), (f) and (i) show the selected area electron diffraction (SAED) patterns of the product obtained at 150, 180, and 250 $^\circ$ C indicating the crystalline nature of the product. The morphology and phase of the as-synthesized samples are found to be highly reproducible, suggesting hydrothermal synthesis as a potential method with the advantages of large-scale production and

low-temperature synthesis. Unlike the individual nanoplates obtained in the present work, Yan *et al.* reported intersectional nanoplates in a solution chemistry route using organic solvent.³⁵ This suggests that an aqueous medium is suitable for obtaining individual nanoplates.

3.3. Structural properties

Fig. 4 shows the XRD patterns of the CuS products hydrothermally synthesized at (a) 150 $^{\circ}$ C, (b) 180 $^{\circ}$ C, and (c) 250 $^{\circ}$ C with varied precursor [Cu(NO₃)₂ and Na₂S₂O₃] molar ratios. The XRD patterns [Fig. 4(A)] of the product obtained with a $[Cu(NO_3)_2:Na_2S_2O_3] = 1:2$ molar ratio at 150 and 180 °C are found to be similar and well-matched to pure hexagonal CuS [JCPDS card No. 00-006-0464]. However, the product obtained at 250 °C shows two additional diffraction peaks [Fig. 4(A)], which are assigned to Cu₂S [JCPDS card No. 00-053-0522] along with the major hexagonal CuS diffraction peaks. We believe that the relatively high pressure generated during the high temperature (250 °C) hydrothermal synthesis leads to the desulfurization of some CuS to Cu₂S. Fig. 4(B) shows the XRD patterns of the product synthesized at (a) 150 °C, (b) 180 °C, and (c) 250 °C with a Cu(NO₃)₂ to Na₂S₂O₃ molar ratio of 1:4. The XRD patterns from the samples synthesized at 150 and 180 °C show the presence of orthorhombic sulfur (JCPDS card no. 04-012-7311) along with CuS. This is obviously due to the excess amount of thiosulfate in the reaction medium. Interestingly, no sulfur is detected in the XRD pattern [pattern (c) of Fig. 4(B)] of the sample prepared at 250 °C with same molar ratio of the precursors. The main reason on the absence of sulfur is due to its degradation above ~ 175 °C, as confirmed by the thermogravimetry (TG) measurement (discussed later). It is important to note that the diffraction peak intensity from sulfur is found to be higher than that from pure CuS in the product obtained at 150 °C and it is slightly reduced for the sample prepared at 180 °C, indicating partial degradation of sulfur. Further increasing the thiosulfate concentration, *i.e.*, 1:6 molar ratio of $Cu(NO_3)_2$ to $Na_2S_2O_3$, we obtained CuS along with sulfur at all three reaction temperatures, as confirmed from the XRD patterns [Fig. 4(C)]. It is believed that the sulfur content in this case is much higher than that obtained with a $[Cu(NO_3)_2:Na_2S_2O_3]$ molar ratio of 1:4 and therefore all of it could not be completely degraded in 8 h even though it was prepared at 250 °C. Moreover, the decrease in the diffraction intensity from elemental sulfur in the XRD spectra with an increase in the synthesis temperature clearly indicates the degradation of sulfur at higher temperatures. This suggests that both the precursor molar concentration and the reaction temperature are crucial for obtaining pure CuS. An optimum precursor $[Cu(NO_3)_2 : Na_2S_2O_3]$ molar ratio of 1:2 is suitable for synthesizing pure CuS in the temperature range of 150–180 °C, whereas with a molar ratio of 1:4, the synthesis temperature should be higher than 200 °C, so the excess sulfur formed could be degraded. However, An et al. reported pure CuS with a 1:6 precursor molar ratio of copper acetate and sodium thiosulfate in ethylene glycol solvent and sodium oleate and hexadecylamine as surfactant at 180 °C.²² This suggests that the present synthesis, in aqueous medium, is suitable for obtaining pure CuS in a shorter reaction time with a lower thiosulfate precursor concentration. The product obtained from a $[Cu(NO_3)_2: Na_2S_2O_3]$ molar ratio of 1:2, in the presence of CTAB, at different temperatures in 8 h show similar XRD patterns as shown in Fig. 4(A), and therefore are not shown.

The formation of CuS from precursors $Cu(NO_3)_2$ and $Na_2S_2O_3$ follows the reactions described in eqn (1) and (2). First, the Cu^{2+} and $S_2O_3^{2-}$ ions are released in the aqueous medium to form $[Cu(S_2O_3)_2]^{2-}$ [eqn (1)]. Upon heating, this complex is converted to CuS through eqn (2). It was confirmed from the acidic pH of the filtrate, due to the formation of H_2SO_4 . Further, it was verified by adding BaCl₂ to the filtrate, which produced a white precipitate of barium sulfate.

$$Cu(NO_3)_2 + 2Na_2S_2O_3 = Na_2[Cu(S_2O_3)_2] + 2NaNO_3$$
 (1)

$$Na_{2}[Cu(S_{2}O_{3})_{2}] + H_{2}O \rightarrow CuS \downarrow + H_{2}SO_{4} + Na_{2}SO_{4} \qquad (2)$$

The above reactions are followed with all the precursor molar ratios used to synthesize CuS in the present work. However, with higher $Na_2S_2O_3$ concentrations, *i.e.*, with a $Cu(NO_3)_2:Na_2S_2O_3$ molar ratio of 1:4 and 1:6, excess thiosulfate remains in the solution. The excess thiosulfate is converted to elemental sulfur during the synthesis [Fig. 4(C)]. This elemental sulfur was present in the product, either along with



Fig. 4 X-ray diffraction patterns of CuS prepared at (a) 150 °C, (b) 180 °C, and (c) 250 °C in 8 h using the hydrothermal technique with a precursor [Cu(NO₃)₂: Na₂S₂O₃] molar ratio of (A) 1:2 (B) 1:4, and (C) 1:6.

CuS or degraded, depending on the precursor molar ratio and the synthesis temperature.

3.4. Thermal property

The presence and degradation of elemental sulfur formed with CuS was further characterized by thermal analysis. Fig. 5(a) and (b) show the thermograms of pure CuS and CuS with S products prepared hydrothermally from copper nitrate and sodium thiosulfate with molar ratios of 1:2 (at 180 °C) and 1:6 (at 150 °C) in 8 h, respectively. The pure CuS, obtained with a molar ratio of 1:2 at 180 °C [Fig. 1(b), Fig. 4(A)-(b)] started to degrade at ~ 280 °C and continued up to ~ 380 °C. A weight loss of $\sim 12\%$ is measured from above degradation [region I, Fig. 5(a)] and is ascribed to the conversion of CuS to Cu₂S [eqn (3)]. If all of the CuS is converted to Cu_2S , we must observe a weight loss of $\sim 17\%$ in the TG curve according to eqn (3). However, a weight loss of $\sim 12\%$, as measured from TG curve, confirms that some of the CuS is utilized in the formation of CuSO₄ (discussed later) thereby simultaneously increasing ~5% of the weight [eqn (4)]. In the temperature range of 380–400 °C (region II), most of the Cu₂S and CuSO₄ can react with air to form copper sulfate hydroxide hydrate and copper sulfate hydroxide [eqn (5)] for which a sharp 28.5% mass gain is observed [Fig. 5(a)]. In the temperature region of 400-470 °C (region III) and until 510 °C (region IV), copper sulfate hydroxide hydrate and copper sulfate hydroxide start degrading to copper oxide sulfate and copper oxide. However, the rate of formation of copper sulfate hydroxide hydrate and copper sulfate hydroxide [eqn (5)] is slightly higher than their degradation [eqn (6)], thereby a minor mass gain occurs [Fig. 5(a) region III & IV], which is continued until the temperature is 600-650 °C. At \sim 650 °C, copper oxide sulfate starts degrading to copper oxide [eqn (7)]. Finally, $\sim 92\%$ of the original mass remains after the thermal treatment of pure CuS, which has completely converted to CuO at 800 °C. In the case of CuS with elemental S [Fig. 5(b)], sulfur starts to degrade at 175 °C and at 315 °C, all the elemental sulfur gets degraded leaving the pure CuS. Above 315 °C, we obtain a similar TG curve to that of pure CuS [Fig. 5(a)].

$$2\mathrm{CuS} + \mathrm{O}_2 = \mathrm{Cu}_2\mathrm{S} + \mathrm{SO}_2 \tag{3}$$



Fig. 5 TG curve of the product obtained with (a) $[Cu(NO_3)_2:Na_2S_2O_3] = 1:2$ molar ratio at 180 °C, and (b) $[Cu(NO_3)_2:Na_2S_2O_3] = 1:6$ molar ratio at 150 °C, using the hydrothermal technique.

$$CuS + O_2 \rightarrow CuSO_4 \tag{4}$$

$$Cu_2S + CuSO_4 + air \rightarrow Cu_3(SO_4)_2(OH)_2 \cdot 4H_2O + Cu_3(SO_4)(OH)_4$$
(5)

$$\operatorname{Cu}_3(\operatorname{SO}_4)_2(\operatorname{OH})_2 \cdot 4\operatorname{H}_2\operatorname{O} + \operatorname{Cu}_3(\operatorname{SO}_4)(\operatorname{OH})_4 \to \operatorname{Cu}_2\operatorname{OSO}_4 + \operatorname{CuO} + \operatorname{H}_2\operatorname{O}_4$$
(6)

$$Cu_2OSO_4 \rightarrow CuO + SO_2$$
 (7)

All the above reaction steps [eqn (3)-(7)] and their products are verified by XRD analysis. Fig. 6 shows the XRD patterns of the as-synthesized pure CuS and the residues of pure CuS calcined at different temperatures for 1 h in presence of air. The diffraction features of the different compounds obtained at different calcined temperature are assigned with respect to the JCPDS cards and marked with symbols. The residue obtained upon calcining pure CuS at 350 °C shows the formation of Cu₂S [JCPDS card no. 00-053-0522] and CuSO₄ [JCPDS card no. 00-015-0775], which is in accordance with the TG analysis [eqn (3) and (4), region I of Fig. 5]. However, the pure CuS product calcined at 400 and 450 °C produced copper sulfate hydroxide hydrate [JCPDS card no. 00-002-0107] and copper sulfate hydroxide [JCPDS card no. 01-076-1621], as shown in Fig. 6. Upon calcining the pure CuS product at 600 °C, copper sulfate hydroxide and its hydrate are converted to copper oxide sulfate [JCPDS card no. 00-046-0005] and copper oxide [JCPDS card no. 01-080-1268]. At a calcination temperature of 800 °C,



 $\ensuremath{\textit{Fig. 6}}$ XRD patterns from the residues of pure CuS calcined at different temperatures in air.

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Fig. 7 EDX spectrum of the pure CuS sample after calcination at 800 $^\circ$ C in air for 1 h, showing the formation of CuO with at% of Cu and O.

copper oxide sulfate is completely converted to CuO [eqn (7)]. Fig. 7 shows an EDX spectrum with an Cu : O atomic ratio of 1.05, indicating the formation of a CuO phase for the sample calcined at 800 °C in air. The formation of different phases, as confirmed from the *ex situ* XRD measurements (Fig. 6), upon calcining pure CuS product in air confirms the reaction steps described above in the TG analysis [Fig. 5 and eqn (3)–(7)].

Furthermore, the thermal stability of pristine CuS prepared with a precursor molar ratio of $[Cu(NO_3)_2:Na_2S_2O_3] = 1:2$ at 180 °C in 8 h was investigated by performing in situ high temperature XRD. The high temperature XRD was performed in a vacuum with Co as the X-ray target. Fig. 8 presents the XRD patterns of pristine CuS collected at different temperatures in a vacuum. As shown earlier, the XRD of the as-synthesized product at room temperature is matched to pure CuS. Upon heating the pristine CuS to 350 °C in a vacuum, a Cu₂S phase emerges. This is in accordance with the thermal analysis [Fig. 5(a)], which shows the desulfurization of CuS to Cu₂S. Upon further increasing the temperature up to 480 °C, the intensity from Cu₂S diffraction features is found to increase, which indicates more desulfurization of CuS to Cu₂S. The XRD pattern collected at 600 °C shows complete conversion of the initial CuS product to Cu₂S (Fig. 8). With further increasing of the temperature up to 800 °C in the current work, the Cu₂S remains stable. Fig. 9 shows an EDX spectrum of the CuS



Fig. 8 XRD patterns of pristine CuS heated at different temperatures in a vacuum. High temperature heating induced the phase change of CuS to Cu_2S.



Fig. 9 EDX spectrum of pristine CuS after annealing at 800 $^{\circ}$ C in a vacuum for 1 h, with the at% of Cu and S suggesting the formation of Cu₂S.

sample after annealing at 800 °C for 1 h in a vacuum with an Cu:S atomic ratio of 1.99, indicating the formation of Cu₂S, as confirmed from the XRD analysis. It is also important to note that the most intense diffraction feature of Cu₂S, at 2θ of ~ 54° , is found to be shifted to a lower 2θ with an increase in the temperature of the sample. This is due to the lattice expansion of the crystal at higher temperatures.

3.5 Optical properties

The optical properties were measured using UV-vis spectrophotometry. The CuS nanoparticles obtained in the presence of CTAB were taken for UV-vis measurements because they were not agglomerated and were found to be easily dispersed in ethanol. Fig. 10(A) shows the plots of $\%T \nu s$. wavelength for the CuS nanoparticles prepared at (a) 150 °C, (b) 180 °C, and (c) 250 °C in the presence of CTAB with a precursor molar ratio of 1:2 $[Cu(NO_3)_2:Na_2S_2O_3]$. A broad peak is observed in the region of 600-650 nm for the CuS prepared at 150 and 180 °C, whereas the CuS prepared at 250 °C shows a peak at ~675 nm. Fig. 10(B)-(D) show the bandgap plots of $(\alpha h\nu)^2 \nu s$. $E(=h\nu)$ as per Tauc's equation $[\alpha h\nu = K(h\nu - E_g)^{1/2}]$ for the direct bandgap material, for CuS prepared at 150, 180 and 250 °C, respectively, [where $\alpha = -\ln T$, h = plank constant, $\nu = \text{frequency}$, $K = \text{constant}, E_{g} = \text{bandgap}]^{.36,37}$ The measured bandgap is 1.75 eV for CuS prepared at 150 °C whereas it is 1.68 eV for CuS prepared at 180 and 250 °C.

The visible region bandgap of copper sulfide promises that it has potential applications in photovoltaics. Wu et al. fabricated a hetero-junction of Cu₂S and CdS on indium-tin-oxide glass and flexible plastic substrates by spin coating to study their photovoltaic performance.9 Lee et al. reported polymer solar cells using Cu₂S-MWCNTs nanocrystals.³⁸ For the photovoltaic application, it is important to fabricate the materials as thin film forms. Copper sulfide thin films can be obtained directly by electrochemical or atomic layer deposition processes.^{39,40} However, a powdered material is commonly spin-coated, or dipcoated or drop-casted to fabricate a thin film. Glass, polyester, and metals are generally used as the substrate for depositing thin films of Cu_xS.⁴¹ We approached here, two methods to fabricate CuS thin films on Si wafer or glass substrates. In the first one, we placed a Si wafer inside the Teflon-lined autoclave and performed the hydrothermal reaction. The reaction was performed using precursors Cu(NO₃)₂ and Na₂S₂O₃ in a 1:2 molar ratio at 180 °C for 8 h in the presence of CTAB. After the reaction,

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Fig. 10 (A) Optical % transmittance plot of CuS prepared at (a) 150 °C, (b) 180 °C and (c) 250 °C in the presence of CTAB. Corresponding bandgap plots of CuS prepared at (B) 150 °C, (C) 180 °C and (D) 250 °C.



Fig. 11 SEM images of CuS film on (a, b) Si (100) substrate, and (c, d) glass substrate.

the Si (100) wafer was removed and the surface morphology was studied by FE-SEM. Fig. 11(a) shows a low-magnification FE-SEM image of the non-uniform CuS film on the Si substrate. Moreover, selected regions of the substrate were found to be uniformly coated with CuS nanoparticles of sizes <100 nm, as shown in Fig. 11(b). In the second approach, we synthesized a CuS powder using the hydrothermal method with precursors $Cu(NO_3)_2$ and $Na_2S_2O_3$ at a 1:2 molar ratio at 150 °C for 8 h. The as-synthesized CuS powder was dispersed in 10 mL dode-canethiol and drop-casted onto a glass substrate. The drop-casted glass sample was dried at 150 °C for 2 h. Fig. 11(c) and (d) show the SEM images of the CuS film drop-casted on the glass substrate at two different magnifications, indicating the uniformity of the film all over the substrate. This suggests that the hydrothermally as-synthesized CuS powder can be

deposited on a suitable substrate by spin-coating or dropcasting, for photovoltaic applications.

4. Conclusions

Here we report the synthesis of CuS using common and inexpensive chemicals in an aqueous medium by a hydrothermal method. The molar concentration ratio of the precursors, i.e., copper nitrate and sodium thiosulfate, and the reaction temperature were found to be important parameters for synthesizing pure CuS. Agglomerated and dispersed nanoparticles/ nanoplates are obtained in the absence and presence of a surfactant in the reaction medium, respectively. The formation mechanism of CuS and other intermediate copper compounds are discussed in detail using thermal analysis and XRD for the first time. The XRD pattern collected from the residue of pure CuS calcined at different temperature in air confirmed the formation of several intermediate products before being completely converted to CuO at 800 °C, which is in accordance with the TG analysis. However, the *in situ* high temperature XRD measurements in a vacuum show complete conversion of CuS to Cu₂S at 600 °C without any intermediate products. The UV-vis absorption measurements show that the bandgap of the CuS nanoparticles are in the range of 1.68-1.75 eV, suggesting potential applications in optoelectronic devices.

Acknowledgements

We gratefully acknowledge the Indian Institute of Technology, Kharagpur for the financial support of this work through an ISIRD grant.

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