Nanocrystalline Copper Selenide formation by Direct Reaction between Cu-ions and Selenosulfate

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Abstract

Copper selenide (Cu_3Se_2) nanocrystals were successfully synthesized on glass substrate by the chemical bath deposition technique. The room temperature formation of Cu_3Se_2 from the reaction between Cu-ions and selenosulfate in aqueous solution was investigated. The resulting precipitate from the reaction of Cu-ions and selenosulfate was initially light green (mainly a mixture of amorphous Cu_2SO_3 , CuSO_3 and $\text{Cu}(\text{OH})_2$) and turned to greenish brown and finally brownish (mainly Cu_3Se_2). Cu_3Se_2 was formed via the hydroxide cluster mechanism and reaction between $\text{Cu}(\text{OH})_2$ and the slowly generated Se^{2-} ions. The Cu_3Se_2 exhibited a disordered phase and small nanocrystals in the range of 2 to 5 nm. The formation mechanism of different phases of copper selenide by chemical bath deposition technique were explained in details.

Keywords: Copper Selenide; Selenosulfate; Reaction; Precipitation.

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1. Introduction

The binary compound semiconductor copper selenide has potential for use in thin film solar cells, window material, optical filter, super ionic conductor, electro-optical devices, thermoelectric converters, microwave shield coatings and transparent layers in high-speed detectors.^[1-3] Copper selenide has been studied with great interest during the past decades because of its potential applications in the fabrication of photovoltaic devices.^[4-8] Many phases and structural forms, i.e., stoichiometric α - Cu_2Se , Cu_3Se_2 , CuSe and CuSe_2 , as well as non-stoichiometric, Cu_{2-x}Se ,^[9] Cu_3Se_2 ,^[10-12] Cu_{2-x}Se ,^[13] CuSe ^[14] and Cu_2Se ^[15-16] compositions of copper selenide have been reported and synthesized via various methods. Copper selenide thin films are mostly found as CuSe , Cu_2Se and Cu_3Se_2 with their bulk materials possessing band gap energies between 1 to 2.3 eV.^[17-21] The thermal stability of these compounds varies depending on their composition. A number of methods have been reported for the deposition of copper selenide thin films such as a flash evaporation, thermolysis of Cu and Se powder

mixtures, the mechanical alloying of Se and Cu in a high-energy ball mill, the reaction of Se with elemental Cu in liquid ammonia, selenisation, solvothermal, vacuum evaporation, hydrothermal,^[22-23] sonochemical,^[24] microwave-assisted heating methods,^[25] solid state reaction, a single-source route and chemical bath deposition (CBD).^[26-28] Among them, CBD is an inexpensive, simple and reproducible deposition technique. The preparative parameters of CBD are easily controllable and give better properties of the films. The oxidation and corrosion of the given substrate do not take place during the reaction.

The reaction between Cu-ions and selenosulfate is the basis of the most commonly used technique for CBD of copper selenide films. These films are composed of micro- and nano- crystals of copper selenide depending on the deposition conditions. Despite considerable amount of work on this system, the exact mechanism of the reaction is not known with certainty. It has been clearly demonstrated that the reaction can proceed through a complexed $\text{Cu}^{2+}/\text{Cu}^+$ with Se^{2-} to form copper selenide. However, whether this reaction involves free (hydro) selenide ions or some complex between the selenosulfate and the Cu species is still an open question. The Cu is normally complexed in the CBD process to prevent the precipitation as well as to control the rate of the overall reaction. In the absence of a complexant for Cu, a precipitate is rapidly formed. A few complex-free reactions have been reported to study the reaction mechanism.^[29-31]

In this paper, complex-free formation of copper selenide quantum dots was studied by transmission electron

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microscopy, X-ray diffraction, and optical spectroscopy. Such a study may help to better understand some aspects of the mechanism of formation of copper selenide in CBD.

2. Experimental section

40 mL of aqueous sodium selenosulfate (Na_2SeSO_3 , ~ 0.01 M Se dissolved in ~ 0.1 M Na_2SO_3) was added dropwise in 40 mL of a 0.1 M aqueous solution of CuSO_4 at room temperature (the pH of the final solution is between 5 and 6). The Na_2SeSO_3 stock solution was prepared by following previously reported procedures.^[32–34] The deposition of copper selenide was carried out on previously cleaned glass substrates with a constant stirring of 300 rpm. The substrates were immersed vertically in the solution. All the experiments were performed at room temperature. After 60-min reaction, the films were taken out of the bath, washed with triple distilled water and dried under Ar flow, whereas the powders were collected from the same bath via filtration.

X-ray diffraction (XRD) patterns of the powders and thin films on glass substrate were recorded on a RINT/PMAX 2500, Rigaku Japan diffractometer operating in the Bragg configuration using $\text{Cu } K_\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The accelerating voltage was set at 50 kV with a current of 300 mA. The scatter and diffraction slits of 1° and a 5-mm collection slit were used. A Technai G2 FEI Hong-Kong Co. Ltd., electron microscope operating at 200 kV was used for transmission electron microscopy (TEM) and electron diffraction (ED) in the selected area mode. The powders scratched from glass substrate were transferred onto carbon-coated copper grids (200 mesh). To simplify the size distribution measurements of crystals, the crystal was treated as a sphere with a radius as the sum estimated by the large axis plus twice the short axis divided by three. The optical transmittance and absorbance spectra of copper-selenide system in a reaction bath and copper selenide thin film were recorded using a Cary 100 UV-Vis spectrophotometer in the range of 350–800 nm.

3. Results and discussion

The selenosulfate solution always contains an excess of sulfite.^[28] The precipitation of copper sulfate and sodium sulfate by adding Na_2SO_3 to a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (at a final pH of 4 to 5) was studied and then the precipitation of copper sulfate and sodium selenosulfate was observed. When $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution (pH ~ 4 to 5, blue color) was mixed with Na_2SO_3 (pH = 8 to 9, colorless) solution, the resultant solution immediately changed from blue to light green (pH = 4 to 5). This color change indicated the formation of copper complexes. These complexes appeared to undergo a series of redox reactions that resulted in an aqueous mixture of Cu^+ , Cu^{2+} , SO_3^{2-} and SO_4^{2-} in equilibrium with a red mixed-valence precipitate of copper known as Chevreul's salt, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$.

When CuSO_4 solution was mixed with Na_2SeSO_3 solution, the same color of precipitation (as that of $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_3$) was observed. The phase of copper complex precipitation was not observed for the as-synthesized precipitate (Fig. 1a) due to its amorphous nature. The precipitate was dried in air ~ 100 °C (Fig. 1b, c). Fig. 1(b and c) shows the XRD patterns

of precipitation collected from the reaction of $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_3$ and $\text{CuSO}_4 \cdot \text{Na}_2\text{SeSO}_3$. Practically, there is no difference between XRD patterns of $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_3$ and $\text{CuSO}_4 \cdot \text{Na}_2\text{SeSO}_3$. This suggests that the initial reactions are almost similar in both cases. Most part of the XRD patterns of these precipitates are similar to PDF 19-0408, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$, Fig. 1(b, c), although it is probable that other forms of CuSO_3 may also exist to some extent. It is noted that $\text{Cu}(\text{OH})_2$ is also seen in the XRD patterns of dried precipitate as shown in Fig. 1b, c. The pattern contains many peaks and they vary considerably in relative intensity from precipitation to precipitation as well as from measurement to measurement for the same sample. This is the situation where copper ions are in dual state, i.e., Cu^{2+} and Cu^+ . The used copper precursor is CuSO_4 , in which Cu is divalent. Attempt to analyze the initial light green suspension formed in the reaction between $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_3$ and $\text{CuSO}_4 \cdot \text{Na}_2\text{SeSO}_3$ by XRD was unsuccessful since we are unable to filter it in the early stage of formation. It turned to light greenish brown. Fig. 1d shows the XRD patterns of a powder collected from the same bath after reaction. Different distinct phases of copper, sulfur, oxygen and selenium are observed in XRD patterns.

Fig. 1 XRD patterns of (a) light brownish precipitate (Initial stage of reaction between CuSO_4 and Na_2SeSO_3 at room temperature) (b) precipitate collected from reaction between CuSO_4 and Na_2SO_3 (precipitate dried in air ~100 °C), (c) precipitate collected from reaction between CuSO_4 and Na_2SeSO_3 (precipitate dried in air ~ 100 °C) and (d) powder collected from the reaction bath of CuSO_4 and Na_2SeSO_3 after 120 min, powder was dried at room temperature for ~ 12 hrs.

The initial light brownish precipitate suggests that it is mainly a mixture of amorphous $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ and $\text{CuOH}/\text{Cu}(\text{OH})_2$, but it could in principle be a copper selenide + $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ and $\text{CuOH}/\text{Cu}(\text{OH})_2$. Therefore, the stages of the reaction can be described as follows:

The most likely pathways for the formation of the copper selenide are as follows: (a) The copper selenide is formed by the reaction of slowly generated Se^{2-} ions with the CuOH or Cu(OH)_2 followed by:

Reaction (6&7) occurs because K_{sp} for copper selenide (10^{-40}) is much smaller than that of CuOH (10^{-14}) or Cu(OH)_2 (10^{-20}); and (b) Hydrolysis of SeSO_3^{2-} to HSe^- . The overall equation for this reaction is generally given as:^[29]

followed by

or (c) complex formation between SeSO_3^{2-} and $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ followed by decomposition of this complex:

Another possible pathway is the reaction between solid Se in water and Cu^{2+} - Cu^+ . Se can be very slightly dissolved in water through a disproportionation reaction to form selenide:

While the concentration of selenide will be extremely low because of the very low solubility product of copper selenide (of the order of 10^{-40}) together with the high concentration of Cu^{2+} , very little selenide is needed to precipitate copper selenide and remove the H_2Se , thereby maintaining the shift in equilibrium to the right. Another possibility is the specific adsorption of $\text{Cu}^{2+}/\text{Cu}^+$ ions at the solid Se surface as the first stage of copper selenide formation.

Although we have followed the development of the formation of copper selenide, we are unable to specify the pathways of copper selenide formation. The main possibilities normally considered are the formation of selenide ions, which react with $\text{CuOH}/\text{Cu(OH)}_2$ and the formation of a complex compound between the selenosulfate and $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$, which was then dissociated to give copper selenide.

The selenosulfate solution is in equilibrium with sulfite and elemental Se:

Se will be precipitated out from this solution if the SO_3^{2-} concentration falls sufficiently. This will occur when $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ and $\text{CuOH} \cdot \text{Cu(OH)}_2$ precipitate at the beginning of the presently investigated reaction. It will also occur if the pH is low (less than 7),^[29] in the present case it is about 5 to 6.

It is more valuable to compare part of this reaction with some reaction. When selenosulphate react with CdSO_4 , then large crystal of CdSO_3 breakdown in the process of forming

CdSe ,^[28] When selenosulphate react with lead carbonate or hydrated lead oxide, then the large crystals of carbonate and hydrated oxide breakdown in the process of forming PbSe ,^[33] the remaining part of reaction observed with hydroxide cluster mechanism.^[26]

Fig. 2 Evolution of the transmission spectra of CuSO_4 and Na_2SeSO_3 reactant mixture with time. Inset shows the evolution of the transmission spectra of CuSO_4 and Na_2SO_3 .

The initially formed suspension is light green and turns to brownish within a few minutes, while gradually precipitates. The suspension and precipitate continue to change color and eventually become brown. These color changes are demonstrated in the transmission spectra of Fig. 2. The same kind of transmission spectra of CuSO_4 - Na_2SO_3 reactant mixture is shown in inset of Fig. 2 for comparison. The same nature of the initial transmission spectra of reactant mixture CuSO_4 - Na_2SO_3 and CuSO_4 - Na_2SeSO_3 was observed, suggesting that the formed material is almost the same (as confirmed from XRD). As the deposition proceeds, the solution composition/phase changes and this can lead to the change in transmission spectra as shown in Fig. 2. There is a gradual red shift of the transmission onset as the reaction proceeds together with the high absorption in ~ 350-500 nm.

Since the initial color change was rapid and the absorption in 350-500 nm is high, a similar kinetic study was also carried out, only using a much more dilute solution (4: 96 times) in order to better see the initial progression. This also reduces the scattering loss as reported by Yocheli and Hodes.^[29] Fig. 3 shows the spectral changes for dilute solutions of CuSO_4 and Na_2SeSO_3 . The gradual blue shift with progressing reaction is seen more distinctly. Fig. 4

shows the XRD patterns of copper selenide on glass substrate after a 60 min reaction time. In the present study, the deposition was carried out several times to get a desired thickness of a material. The XRD patterns of the copper selenide on the glass (after 60 min reaction time) show that the copper selenide was nano-crystalline and a mixture of Cu_2Se , $\text{Cu}_{1.8}\text{Se}$, and CuSe_2 . (211) and (311) reflections were recorded for Cu_2Se and (603) for CuSe . The broad hump in the XRD pattern is due to a poor crystalline nature of copper selenide material and amorphous glass substrate. This suggests a large part of the $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ and $\text{Cu}(\text{OH})_2$ has been converted to copper selenide.

Fig. 3 Evolution of the transmission spectra when CuSO_4 and Na_2SeSO_3 concentration was diluted as 4: 96 with time.

Fig. 4 XRD patterns of copper selenide on glass substrate after reaction time of 60 min.

A TEM study of the copper selenide quantum dots scratched from glass substrate shows that it is comprised mainly of crystals between 2 to 5 nm (Fig. 5) and more concentrations of small crystals. We calculated the average crystallite size for six crystals and it was observed to be 4.4 nm. The lattice spacing of the crystals is consistent with those of copper selenide. A close look at particular crystals shows that it is surrounded by amorphous crystals. This indicates that the formation mechanism of copper selenide is partly an exchange of Se with sulfite at the $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ surface and part reaction of Se^{2-} with $\text{Cu}(\text{OH})/\text{Cu}(\text{OH})_2$ to give copper selenide, which breakdown from amorphous grains and crystallizes.

Fig. 5 High-resolution TEM micrograph of the copper selenide after 60 min reaction scratched from the glass substrate and size distribution of the crystals in this material.

4. Conclusion

In this paper, we investigated the formation of copper selenide nanocrystal from selenosulfate solutions, showing how the initially formed mixture of amorphous $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ and $\text{Cu}(\text{OH})_2$ is converted into copper selenide. The XRD analysis of the copper selenide onto glass substrate showed that the copper selenide were nano-crystalline and mixture of Cu_2Se , $\text{Cu}_{1.8}\text{Se}$, CuSe_2 . Different pathways than usually considered for the formation of copper selenide from selenosulfate have been suggested under certain reaction conditions. A TEM study of the copper selenide shows that it is comprised mainly of crystals between 2 to 5 nm. The spectral changes of the precipitate formed during the reaction correlated with phase/composition of the material.

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Supporting information

Not applicable

Conflict of interest

There are no conflicts to declare.

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