Non-stoichiometric Cu₃S Hexagonal Nanoplates: Synthesis, Characterization and Electrochemical Properties

Jiang Jia-Xing*¹, Zheng Yuan-Hui², Zhao Jian-Xi*¹

¹(College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, 350108)
²(Materials Engineering, Monash University, Clayton, VIC, Melbourne 3800, Australia)

Abstract: Non-stoichiometric copper sulfide (Cu₃S) hexagonal nanoplates were synthesized through a simple refluxing method using ethylene glycol (EG) and poly(N-vinyl-2-pyrrolidone) (PVP) as solvent and capping agent, respectively. The as-synthesized samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Vis spectroscopy and cyclic voltammetry (CV). TEM observations show hexagonal plate morphology of the as-synthesized samples. XRD results show that the products evolve from covellite CuS to digenite Cu₁₃S with the increase of Cu/S molar ratio. In addition, it is found that the optical and electrochemical properties of the as-synthesized samples change remarkably with the variation of their composition.

Key words: Cu₃S; nanoplate; electrochemical properties

In recent years, transition metal chalcogenide have been extensively studied due to their unique electrical, magnetic and optical properties. Non-stoichiometric copper sulfide (Cu₃S, x=1-2), a typical representative of transition metal chalcogenide, involves various stable phases at room temperature, such as covellite (CuS) in the “sulfur-rich region”; and anilite (Cu₁₃S), digenite (Cu₁₃S), djurleite (Cu₁₉S), and chalcocite (CuS) in the “copper-rich region” [1]. Cu₃S compounds in different stoichiometries have widespread potential applications, such as solar cells[9,10], photothermal conversion of solar energy[11], superionic materials[12,13], and chemical sensor[14]. In addition, Cu₃S has been demonstrated as a potential nanometer-scale switch[15].

(Received date: 2009-02-16, Revised date: 2009-04-03.

*Corresponding author. E-mail: jxzhao.colloid@fzu.edu.cn

First author: Jiang Xing, male, 28, Doctorate student; research direction: colloid and interface chemistry.)
Stimulated by promising applications of Cu$_2$S nanocrystals, the preparations of them have attracted tremendous interest recently. Various methods such as solid-state reactions $^{[9]}$, template-controlled $^{[10]}$, microemulsion-directed $^{[11]}$, hydrothermal $^{[12]}$ and solvothermal methods $^{[13]}$, have been utilized in preparing the well-defined superstructures (e.g., nanoparticles $^{[14,15]}$, rods $^{[16,17]}$, wires, flakes $^{[18]}$, plates $^{[19-21]}$, or hollow spheres $^{[22]}$, etc.). Most of these studies focus on controlling synthesis of special morphologies of Cu$_2$S(x=1 or 2). However, very few systematic studies have been performed on the correlation between the structure and optical/electrochemical properties of non-stoichiometric copper sulfides (Cu$_2$S).

Herein, we report a facile and efficient method to synthesize Cu$_2$S hexagonal nanoplates, using ethylene glycol (EG) as a solvent as well as a weak reducing agent. An oriented aggregation and Ostwald ripening growth mechanisms have been discussed. Moreover, the optical absorption and electrochemical behavior of these materials were also investigated in detail, and the results exhibit that both optical and electrochemical behavior are dependent on their composition (i.e., the stoichiometry of Cu and S).

1 Experimental

1.1 Synthesis

In a typical procedure, 0.199 g (1 mmol) cupric acetate monohydrate and 0.6 g poly(N-vinyl-2-pyrrolidone) (PVP, $M_w=3000$, 2x10$^{-2}$ mmol) were dissolved in 30 mL of ethylene glycol (EG) solvent to form a clearly transparent solution. Subsequently, a certain amount of sulfur powder was added to the above solution under vigorous stirring. Then the mixture was transferred into a 100 mL flask and refluxed at 200 °C for 5 h (the detailed experimental conditions are listed in Table 1). After completion of the reaction, the flask was cooled down to room temperature naturally. The resulting precipitates were centrifuged, washed thoroughly with pure ethanol, and finally dried in air at room temperature. The obtained samples were denoted as sample 1–5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio of reactants (Cu:S)</th>
<th>Reaction temperature / °C</th>
<th>Reaction time / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:0:1.0</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1:2:1.0</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>1.5:1.0</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>1.8:1.0</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>2:0:1.0</td>
<td>200</td>
<td>5</td>
</tr>
</tbody>
</table>

1.2 Characterizations

XRD patterns of the samples were recorded by a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 0.154 18 nm). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The data were recorded at a scan rate of 0.02°·s$^{-1}$ in the 2θ range of 10° to 80°. The microstructures and morphologies were observed by Tecnai G2 F20 Field Emission Transmission Electron Microscope (TEM) working at 200 kV. UV-Vis diffuse reflectance spectra (DRS) were recorded on UV-Vis-NIR spectrometer (Lambda 900, Pekin-Elmer).

Electrochemical measurements (cyclic voltammetry) were performed by using a CHI 660C electrochemical workstation system. The Cu$_2$S was coated on the glassy carbon disk electrode surface by depositing 10 μL of 20 mg·mL$^{-1}$ Cu$_2$S ethanol suspension with 0.02% Nafion solution and then dried in air. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and the counter electrode, respectively. The electrolyte solution was 0.05 mol·L$^{-1}$ disodium tetraborate decahydrate solution with pH=9.2. Cycles were performed from 0.2 to −1.2 V (negative-going potential scan), then to +0.2 V (positive-going potential scan), all versus SCE at a scan velocity of 5 mV·s$^{-1}$.

2 Results and discussion

The XRD patterns of the as-synthesized samples with different Cu:S molar ratios are shown in Fig.1. When the molar ratio of Cu and S is 1:0:1.0, the diffrac-
Fig. 1 XRD patterns of the as-synthesized samples

tion peaks of the as-prepared sample are in good agreement with the hexagonal phase of the covellite structure with the P6_{3}mmc space group (PDF No. 78-2121), as shown in Fig. 1a. With the increase of Cu/S molar ratio, Cu_{13}S phase is observed (Fig. 1b~c). The diffraction patterns clearly show two sets of diffraction peaks, indicating that these samples are composite materials containing Cu_{12.8}S (0 ≤ δ < 0.8) and Cu_{13}S. When the molar ratio of Cu and S is 2.0:1.0, all diffraction peaks in Fig. 1e match those of rhombohedral digenite Cu_{13}S (PDF file No. 23-0962).

Since no strong reductant (e.g., potassium borohydride or hydrazine hydrate) is used in the experiments, it is believed that the EG solvent is acted as a weak reducing agent. The reduction potential for Cu^{2+}/Cu is higher than that of S/H_{2}S (reduction potential: E^{0} = 0.342 V for Cu^{2+} + 2e→Cu; E^{0} = 0.142 V for S + 2H^{+} + 2e→H_{2}S), so the essence of the reaction is reduction of copper ions but not sulfur powder (S) by EG at appropriate temperature. Thus, the chemical reactions are proposed as follows:

\[ 2\text{HOCH}_{2}\text{CH}_{2}\text{OH} = 2\text{CH}_{3}\text{CHO} + \text{H}_{2}\text{O} \quad (1) \]

\[ 2\text{CH}_{3}\text{CHO} + \text{Cu(\text{CH}_{2}\text{COO})}_{2} \rightarrow \text{Cu} + 2\text{CH}_{3}\text{COOH} + \text{Cu} \quad (2) \]

\[ \text{Cu} + \text{S} = \text{CuS} \quad (3) \]

\[ \text{CuS} + \text{Cu} = \text{Cu}_{13}\text{S} \quad (4) \]

TEM observations of sample 1 and 5 are shown in Fig. 2. Typical low-magnified TEM images of these two samples (Fig. 2a and b) show that both consist almost entirely of the hexagonal nanoplates and indicate that the architecture of hexagonal nanoplates can be successfully synthesized on a large scale. Also, many dimer-plate structures (highlighted by circles) can be observed. The magnified TEM images (the inset in Fig. 2a and b) indicate that the dimer-plate structure is composed of two vertical hexagonal plates. The average diameter of the hexagonal plates is about 500 nm, and the thickness is about 50 nm and 100 nm for sample 1 and sample 5, respectively.

Fig. 3 presents the UV-Vis absorption spectra of the Cu_{13}S nanocrystals. For the as-synthesized Cu_{13}S nanocrystals, its absorption peak centers at 675 nm (Fig. 3-1), which is in good agreement with that reported by Gong [18]. For sample 5, the corresponding absorption peak locates at 1001 nm. The peak position of the samples was listed in Fig. 3. It is obvious that the absorption peak of the as-synthesized samples shifts from 675 nm
to 1 001 nm with the Cu/S molar ratio increasing. Based
on the above XRD results, the red shift of the absorption
peak in Fig.3 should be attributed to the evolution
of the composition of the as-synthesized samples.

Fig.4 shows the cyclic voltammetry curves of Cu$_x$S
in buffer borate solution of pH=9.2. In the voltam-
ograms, the reduction peak potential (peak I) shifts from
-0.830 V (sample 1) to -0.697 V (sample 5, versus SEC)
with the increasing Cu/S molar ratio, and the current
increases rapidly from -1.1 V to -1.2 V. There are
three oxidation peaks which are at about -0.850 V (peak II),
-0.108 V (peak III), and +0.05 V (peak IV), respec-
tively.

The peak I attributes to the reduction of the non-stoichio-
metric Cu$_x$S into Cu$_2$S according to the reaction:

\[ 2\text{Cu}_x\text{S} + (2-x)\text{H}_2\text{O} + (4-2x)e^- \rightarrow \]
\[ x\text{Cu}_2\text{S} + (2-x)\text{OH}^- + (2-x)\text{HS}^- (1 \leq x \leq 1.8) \quad (5) \]

As shown in the XRD results, there are only two
phases (CuS and Cu$_{1.5}$S) in the as-synthesized samples,
so the essence of the reaction (5) is reduction of CuS and
Cu$_{1.5}$S to Cu$_2$S:

\[ 2\text{Cu}_{1.5}\text{S} + 0.2\text{H}_2\text{O} + 0.4e^- \rightarrow \]
\[ 1.8\text{Cu}_2\text{S} + 0.2\text{OH}^- + 0.2\text{HS}^- \quad (6) \]
\[ 2\text{CuS} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cu}_2\text{S} + \text{OH}^- + \text{HS}^- \quad (7) \]

Because digenite Cu$_{1.5}$S dominates gradually in the
as-synthesized samples with the Cu/S molar ratio in-
creasing as shown in Fig.1, the potential of the peak I
becomes more positive, which agrees with the UV-Vis
results.

The rapid increase in current at the end of the
negative potential scan should be related to copper re-
duction according to the reaction (5):

\[ \text{Cu}_2\text{S} + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Cu} + \text{OH}^- + \text{HS}^- \quad (8) \]

Whereas the reaction at oxidation peak II should
be ascribed to reverse process of reaction (8), provided
that the HS$^-$ required for this reaction remains in the
vicinity of the interface.

The peak III and peak IV probably relate to copper
sulphide electro-oxidation going through all possible
non-stoichiometric sulphides with correlative formation
of Cu(II), according to the sequence (22):
\[
\text{CuS} \rightarrow \text{Cu}_{1+x}\text{S} + \text{Cu(II)} \text{ species}
\]

\[
\rightarrow \text{Cu}_{1+\delta}\text{S} + \text{Cu(II)} \text{ species}
\]

\[
\rightarrow \text{Cu}_{1+\beta}\text{S} + \text{Cu(II)} \text{ species}
\]

\[
\rightarrow \text{CuS} + \text{Cu(II)} \text{ species}
\]

It can be expressed as:
\[
\text{CuS} + 2\varepsilon\text{OH}^- \rightarrow \text{Cu}_{2+\varepsilon}\text{S} + x\text{CuO} + x\text{H}_2\text{O} + x\epsilon^-(9)
\]

3 Conclusions

Non-stoichiometric copper sulfide hexagonal nanoplates were successfully synthesized through a simple refluxing method. With the increase of Cu/S molar ratio, the composition of the as-synthesized samples evolves from covellite CuS to digenite Cu$_{1+x}$S, the absorption peak shifts from 675 nm to 1 001 nm and the peak potential for reduction of Cu$_x$S to Cu$_y$S shifts towards the positive potential direction.

References: