

## 六边形非化学计量比 $\text{Cu}_x\text{S}$ 纳米片:合成、表征及电化学性质

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**摘要:** 分别采用乙二醇(EG)和聚乙烯吡咯烷酮(PVP)为溶剂和模板剂,用简单的回流方法合成六角型非化学计量比  $\text{Cu}_x\text{S}$  纳米片。并用 X 射线衍射(XRD)、透射电子显微镜(TEM)、紫外可见近红外光谱仪(UV-Vis)、循环伏安法(CV)对产物进行表征。TEM 研究表明样品形貌为纳米六角片。XRD 结果表明,随着 Cu/S 物质的量比的逐渐增加,样品物相从靛铜矿(covellite) $\text{CuS}$  逐渐转变为蓝辉铜矿(digenite) $\text{Cu}_{1.8}\text{S}$ 。此外,随着样品组分的变化,其光学和电化学性质均发生显著变化。

**关键词:**  $\text{Cu}_x\text{S}$ ; 纳米片; 电化学性质

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## Non-stoichiometric $\text{Cu}_x\text{S}$ Hexagonal Nanoplates: Synthesis, Characterization and Electrochemical Properties

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**Abstract:** Non-stoichiometric copper sulfide ( $\text{Cu}_x\text{S}$ ) 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  $\text{CuS}$  to digenite  $\text{Cu}_{1.8}\text{S}$  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:**  $\text{Cu}_x\text{S}$ ; 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 ( $\text{Cu}_x\text{S}$ ,  $x=1-2$ ), a typical representative of transition metal chalcogenide, involves various stable phases at room temperature, such as covellite( $\text{CuS}$ ) in the “sulfur-rich region”; and anilite( $\text{Cu}_{1.75}\text{S}$ ), digenite

( $\text{Cu}_{1.8}\text{S}$ ), djurleite( $\text{Cu}_{1.95}\text{S}$ ), and chalcocite( $\text{Cu}_2\text{S}$ ) in the “copper-rich region”<sup>[1]</sup>.  $\text{Cu}_x\text{S}$  compounds in different stoichiometries have widespread potential applications, such as solar cells<sup>[2,3]</sup>, photothermal conversion of solar energy<sup>[4]</sup>, superionic materials<sup>[5,6]</sup>, and chemical sensor<sup>[7]</sup>. In addition,  $\text{Cu}_x\text{S}$  has been demonstrated as a potential nanometer-scale switch<sup>[8]</sup>.

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Stimulated by promising applications of  $\text{Cu}_x\text{S}$  nanocrystals, the preparations of them have attracted tremendous interest recently. Various methods such as solid-state reactions<sup>[9]</sup>, template-controlled<sup>[10]</sup>, microemulsion-directed<sup>[11]</sup>, hydrothermal<sup>[12]</sup> and solvothermal methods<sup>[13]</sup>, have been utilized in preparing the well-defined superstructures (e.g., nanoparticles<sup>[14,15]</sup>, rods<sup>[16,17]</sup>, wires, flakes<sup>[18]</sup>, plates<sup>[19-21]</sup>, or hollow spheres<sup>[12]</sup>, etc.). Most of these studies focus on controlling synthesis of special morphologies of  $\text{Cu}_x\text{S}$  ( $x=1$  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( $\text{Cu}_x\text{S}$ ).

Herein, we report a facile and efficient method to synthesize  $\text{Cu}_x\text{S}$  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 6 g(1 mmol) cupric acetate monohydrate and 0.6 g poly(*N*-vinyl-2-pyrrolidone) (PVP,  $M_w=3\ 000$ ,  $2\times 10^{-2}$  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 1** Experimental conditions of the obtained  $\text{Cu}_x\text{S}$  nanoplates

| Sample | Molar ratio of reactants(Cu:S) | Reaction temperature / °C | Reaction time / h |
|--------|--------------------------------|---------------------------|-------------------|
| 1      | 1.0:1.0                        | 200                       | 5                 |
| 2      | 1.2:1.0                        | 200                       | 5                 |
| 3      | 1.5:1.0                        | 200                       | 5                 |
| 4      | 1.8:1.0                        | 200                       | 5                 |
| 5      | 2.0:1.0                        | 200                       | 5                 |

### 1.2 Characterizations

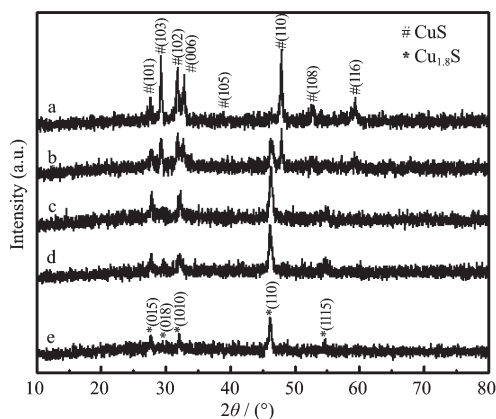
XRD patterns of the samples were recorded by a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu  $K\alpha$  radiation( $\lambda=0.154\ 18\ \text{nm}$ ). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The data were recorded at a scan rate of  $0.02^\circ\cdot\text{s}^{-1}$  in the  $2\theta$  range of  $10^\circ$  to  $80^\circ$ . 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  $\text{Cu}_x\text{S}$  was coated on

the glassy carbon disk electrode surface by depositing  $10\ \mu\text{L}$  of  $20\ \text{mg}\cdot\text{mL}^{-1}$   $\text{Cu}_x\text{S}$  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  $0.05\ \text{mol}\cdot\text{L}^{-1}$  disodium tetraborate decahydrate solution with pH=9.2. Cycles were performed from 0.2 to  $-1.2\ \text{V}$ (negative-going potential scan), then to  $+0.2\ \text{V}$ (positive-going potential scan), all versus SCE at a scan velocity of  $5\ \text{mV}\cdot\text{s}^{-1}$ .

## 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-

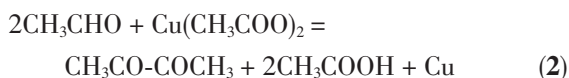
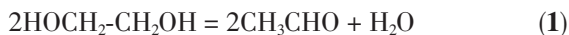


a: sample 1; b: sample 2; c: sample 3; d: sample 4; e: sample 5

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,  $\text{Cu}_{1.8}\text{S}$  phase is observed (Fig.1b~c). The diffraction patterns clearly show two sets of diffraction peaks, indicating that these samples are composite materials containing  $\text{Cu}_{1+\delta}\text{S}$  ( $0 \leq \delta < 0.8$ ) and  $\text{Cu}_{1.8}\text{S}$ . When the molar ratio of Cu and S is 2.0:1.0, all diffraction peaks in Fig.1e match those of rhombohedral digenite  $\text{Cu}_{1.8}\text{S}$  (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  $\text{Cu}^{2+}/\text{Cu}$  is higher than that of  $\text{S}/\text{H}_2\text{S}$  (reduction potential:  $E^\ominus = 0.342$  V for  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ;  $E^\ominus = 0.142$  V for  $\text{S} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}$ ), 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:



TEM observations of sample 1 and 5 are shown in Fig.2. Typical low-magnified TEM images of these two samples (Fig.2a and 2b) show that both consist almost entirely of the hexagonal nanoplates and indicate that

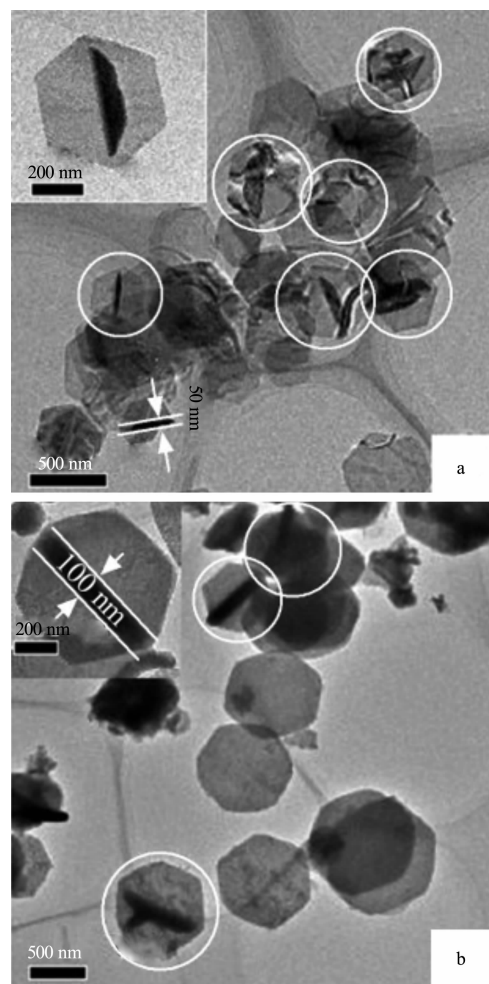


Fig.2 TEM images of the as-synthesized sample 1 (a) and 5 (b)

the architecture of hexagonal nanoplate 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  $\text{Cu}_x\text{S}$  nanocrystals. For the as-synthesized  $\text{CuS}$  nanocrystals, its absorption peak centers at 675 nm (Fig. 3-1), which is in good agreement with that reported by Gong<sup>[18]</sup>. For sample 5, the corresponding absorption peak locates at 1 001 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

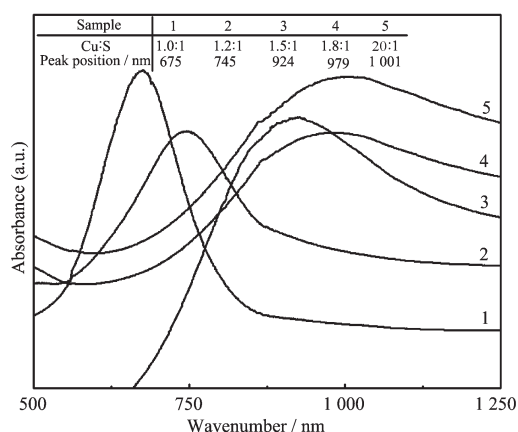
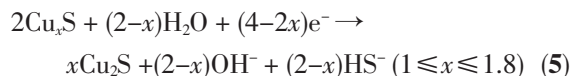


Fig.3 Absorption spectra of the as-synthesized samples

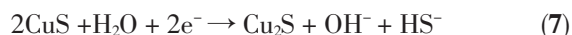
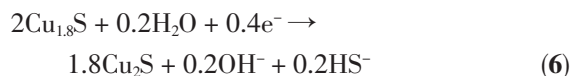
to 1001 nm with the Cu/S molar ratio increasing. Based on the above XRD results, the red shift of the absorption peak in Fig.3 should be attributed to the evolution of the composition of the as-synthesized samples.

Fig.4 shows the cyclic voltammetry curves of  $\text{Cu}_x\text{S}$  in buffer borate solution of pH=9.2. In the voltammograms, the reduction peak potential (peak I) shifts from -0.830 V (sample 1) to -0.697 V (sample 5, versus SEC) with the increasing the 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), respectively.

The peak I attributes to the reduction of the non-stoichiometric  $\text{Cu}_x\text{S}$  into  $\text{Cu}_2\text{S}$  according to the reaction:



As shown in the XRD results, there are only two phases ( $\text{CuS}$  and  $\text{Cu}_{1.8}\text{S}$ ) in the as-synthesized samples, so the essence of the reaction (5) is reduction of  $\text{CuS}$  and  $\text{Cu}_{1.8}\text{S}$  to  $\text{Cu}_2\text{S}$ :



Because digenite  $\text{Cu}_{1.8}\text{S}$  dominates gradually in the as-synthesized samples with the Cu/S molar ratio increasing 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

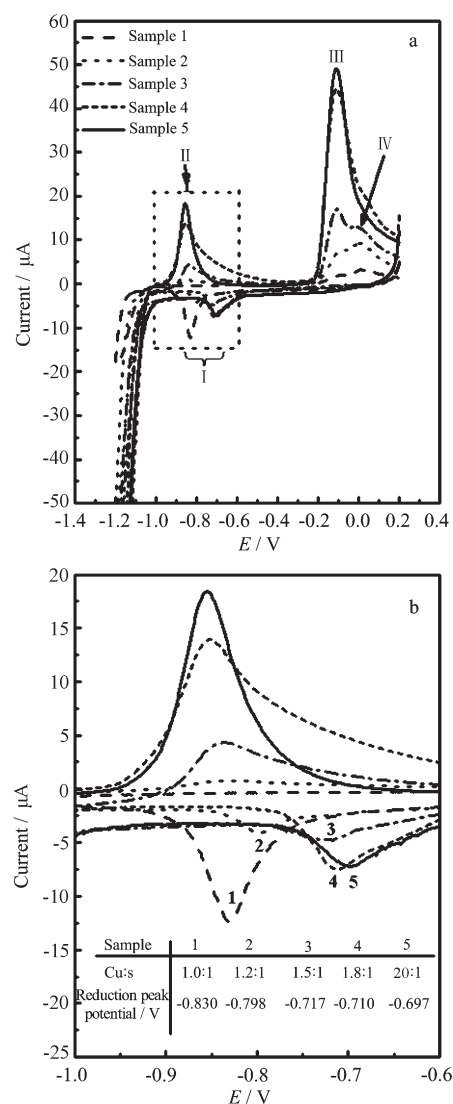
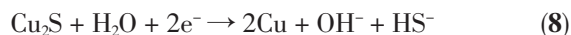


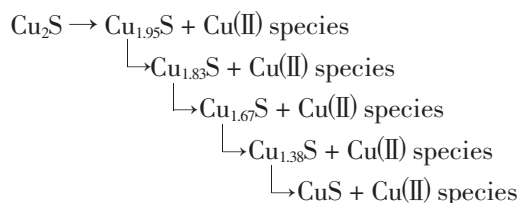
Fig.4 Cyclic voltammograms of the as-synthesized samples in alkaline borax solution of pH=9.2 at room temperature recorded at  $5 \text{ mV} \cdot \text{s}^{-1}$ , Fig.4b is magnified image from the rectangular area in Fig.4a

negative potential scan should be related to copper reduction according to the reaction<sup>[22]</sup>:

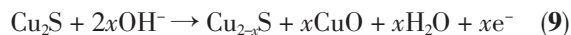


Whereas the reaction at oxidation peak II should be ascribed to reverse process of reaction (8), provided that the  $\text{HS}^-$  required for this reaction remains in the vicinity of the interface.

The peak III and peak IV probably relate to copper sulphide electro-oxidation going through all possible non-stoichiometric sulphides with correlative formation of  $\text{Cu(II)}$ , according to the sequence<sup>[22]</sup>:



It can be expressed as:



### 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  $\text{Cu}_{1.8}\text{S}$ , the absorption peak shifts from 675 nm to 1 001 nm and the peak potential for reduction of  $\text{Cu}_x\text{S}$  to  $\text{Cu}_2\text{S}$  shifts towards the positive potential direction.

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