

Synthesis of covellite (CuS) from the elements

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Abstract

A one-step, corrosion-assisted reaction was developed to synthesize copper sulfide (CuS) from elemental copper and sulfur in water at 60 °C. The as-prepared polycrystalline CuS consists of polyhedral-shaped 2–3 μm crystallites. CuS forms by the oxidation of copper metal in the presence of sulfur, whereas in the presence of water, a continuous solid-state reaction occurs without passivation by the product.

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1. Introduction

The copper sulfide system has been studied extensively owing to its importance in the fields of mineralogy, geology, and corrosion science. Copper sulfides exist in a wide variety of compositions, ranging from copper-rich chalcocite (Cu₂S) to copper-deficient villamaninite (CuS₂) with other intermediate compounds, in-between, such as covellite (CuS), djurleite (Cu_{1.95}S), and anilite (Cu_{1.75}S), among others. Over the last several decades, multiple potential technological applications of copper sulfides have been reported. For example, copper sulfides with copper vacancies in the lattice have been studied extensively for their application as p-type semiconductors in optoelectronic materials, such as solar cells. CuS, a metallic conductor that undergoes transitions to a superconductor below 1.6 K [1], has attracted interest in recent years owing to its potential application in catalysis [2], photovoltaics [3], and cathode materials [4].

Covellite (CuS), the focus of this work, is a stoichiometric compound that is stable up to a temperature of ~500 °C, above

which it decomposes peritectically into Cu_{2–x}S and liquid [5]. According to the phase diagram, excess copper or sulfur results in the formation of secondary anilite (Cu_{1.75}S) phase or sulfur phase, respectively. However, phase relations are complicated as metastable phases, such as “blue-remaining covellite” of composition Cu_{1.1}S, have been reported previously [6]. CuS crystallizes into a unique, hexagonal structure (space group *P6₃/mmc*) [7]. In this structure, both copper and sulfur atoms adopt two distinct coordination environments [8]. As shown in Fig. 1, two-thirds of the copper atoms are at the center of corner-sharing sulfur tetrahedra, which extend into a two-dimensional layer perpendicular to the *c*-axis. These two-dimensional sheets are linked by sulfur atoms present as S₂ dimers. The remaining one-third of copper atoms is at the center of a triangle of sulfur atoms.

Numerous synthetic methods have been reported to yield polycrystalline CuS materials of various structural and microstructural forms, with recent emphasis on nanostructures. Although copper sulfides can be synthesized by a reaction between elemental copper and sulfur [5], direct reactions of the elements at low temperatures (<150 °C) do not proceed completely, but are restricted to the surface of the copper particles because CuS surface layers act as a passivating layer that prevents further reaction. As summarized by Blachnik and

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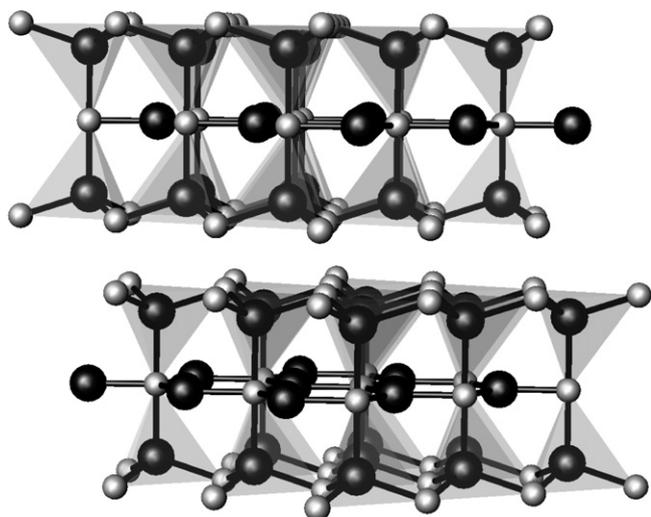


Fig. 1. Schematic representation of the covellite (CuS) structure shown perpendicular to the *c*-axis. For clarity, the S–S bonds that connect each layer are not shown. Black and gray spheres represent copper and sulfur atoms, respectively.

Muller [5], complete reaction of the elemental reagents thus requires a solvent [9,10], higher temperatures to increase the rate of diffusion [11], continuous reactant milling to remove the passive layer [5,12], or slow aging in an inert atmosphere at low temperatures to provide more time for diffusion to occur.

The synthesis of CuS is not limited to solid-state reactions. In recent years, alternative syntheses, including γ -radiation [13], sonochemical [14], microwave irradiation [15], hydrothermal [16], and solvothermal reactions [17,18], have been pursued primarily for the preparation of low-dimensional CuS nanocrystals. These reactions incorporate soluble copper and sulfur reagents into a solvent to lower the reaction temperature, which in combination with a complexing agent controls the morphology of the CuS product. With respect to solvent, Tang et al. reported that solvothermal reactions yield different arrangements of flake-like CuS product crystallites, and that the specific arrangement of these crystallites varies with reaction solvent and temperature [19]. While an ethylene glycol solvent aggregates the flakes into a “flower-like” CuS product (i.e., a sphere similar in appearance to a carnation), an aqueous solvent results in the flakes assembling into “trepan-like” CuS morphologies (i.e., a tube-like particle). Later, the same group reported that an increase in temperature of the hydrothermal reaction yields hollow CuS spheres [17]. Complexing agents and surfactants, such as triethylamine (TEA), cetyltrimethylammonium bromide (CTAB), and ethylenediaminetetraacetic acid (EDTA), also have been used to influence the size and morphology of the CuS product. For example, the addition of the surfactant CTAB to a CuCl_2 and CS_2 reaction changes the morphology of the CuS product from small spheres to “urchin-like” or “snowflake-like” particles in a pure ethanol or ethanol/water reaction solvent, respectively [18].

To avoid the use of toxic H_2S , most liquid phase reactions employ an alternate sulfur source, which decomposes to H_2S , elemental sulfur, or sulfide ions in situ under the reaction

conditions (e.g., hydrothermal water, sonication, γ -radiation). For example, micro-crystalline CuS was synthesized by the reaction of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and various copper sources (CuO , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) at 130–170 °C by Zhang et al. [20,21]. In this reaction, reactive sulfur is generated by the rapid disproportionation of the thiosulfate anion ($\text{S}_2\text{O}_3^{2-}$), which decomposes in water to generate SO_4^{2-} and a mixture of S, H_2S , and H_2S_n . Organic sulfur precursors (e.g., thiourea and thioacetamide) that decompose on heating to form H_2S are used commonly as well. Furthermore, in these reports, copper salts and/or copper organic complexes were used as starting materials, all of which are ultimately synthesized from elemental copper or copper oxides. In this study using only the simplest starting materials, we report that CuS can be prepared from elemental copper and sulfur under aqueous conditions. This preparation substitutes water for the non-aqueous solvents (e.g., acetonitrile, carbon disulfide) used previously in low temperature reactions involving elemental copper and sulfur [9,10]. The addition of water to the solid-state reaction avoids the passivation of the reactive copper surface, which impedes the low temperature, non-aqueous solid-state reaction. Moreover, this work illustrates that recognizing the importance of corrosion processes can aid in the synthesis of simple inorganic solids.

2. Experimental

2.1. Synthesis

Elemental copper (0.01 mol) and sulfur (0.01 mol) powders were weighed and then ground together in an agate mortar. The elemental mixture was then transferred along with 20 mL of distilled water to a 50 mL Teflon-lined pressure vessel, which was then sealed. Multiple experiments were next conducted at reaction temperatures ranging from 60 to 180 °C (at 30 °C intervals) for reaction times of 1, 10, or 60 h to investigate the effect of both reaction temperature and time on the product yield. To investigate the role of oxygen in the reaction, several experiments were repeated in an oxygen-free environment by sealing the pressure vessel under an argon atmosphere and using oxygen-free water. Upon completion of the heating profile, the pressure vessel was allowed to cool naturally to room temperature. The precipitates were then collected by filtration and washed with distilled water several times. After drying in a desiccator for 12 h, the product powders were collected for characterization.

2.2. Characterization

Powder X-ray diffraction (XRD) data were acquired with Cu $K\alpha$ radiation on a Rigaku RINT2000 diffractometer equipped with a graphite monochromator. The morphology and particle size of the products were characterized by scanning electron microscopy (SEM) using a JEOL JSM5610 system. A Horiba EMAX-5770 energy dispersive X-ray fluorescence spectrometer (EDX) was used to evaluate the compositions of the products.

3. Results

The color of all products is deep blue, consistent with the color of the CuS mineral covellite. All the products were weighed and the yields were found to be essentially stoichiometric with only minor losses owing to transfer (>95% based on copper). Fig. 2 shows the XRD profiles of selected reaction products. Under all conditions, copper metal reacts with sulfur to form CuS. The powder X-ray diffraction patterns of the product can be indexed as CuS (JCPDS 06-0464, $a = 3.792 \text{ \AA}$, $c = 16.344 \text{ \AA}$, space group $P6_3/mmc$) with a hexagonal unit cell. With the exception of the product obtained for a reaction temperature of $60 \text{ }^\circ\text{C}$ for 1 h, no reflections indicating the presence of an alternate phase are observed even with no purposeful removal of trace oxygen for the reaction. As shown in Fig. 2(e), the powder XRD pattern of the sample obtained at $60 \text{ }^\circ\text{C}$ for a 1 h reaction time in air indicates the presence of elemental sulfur and Cu_2O along with those of CuS. As shown in Fig. 2(d), these alternate phases disappear when the reaction at $60 \text{ }^\circ\text{C}$ is conducted for 10 h. Overall, the more intense peaks observed for higher reaction temperatures and longer reaction times indicate that the crystallinity of the products increases substantially with temperature and/or longer reaction times (Fig. 2). The energy dispersive X-ray (EDX) analysis of the sample obtained by reaction at $180 \text{ }^\circ\text{C}$ for 10 h indicates that the sample contains only copper and sulfur at an average Cu:S atomic ratio 1.01(11), confirming the stoichiometry of CuS.

4. Discussion

Water clearly plays the crucial role in the formation of pure CuS phase here because it alters the conditions of the solid-

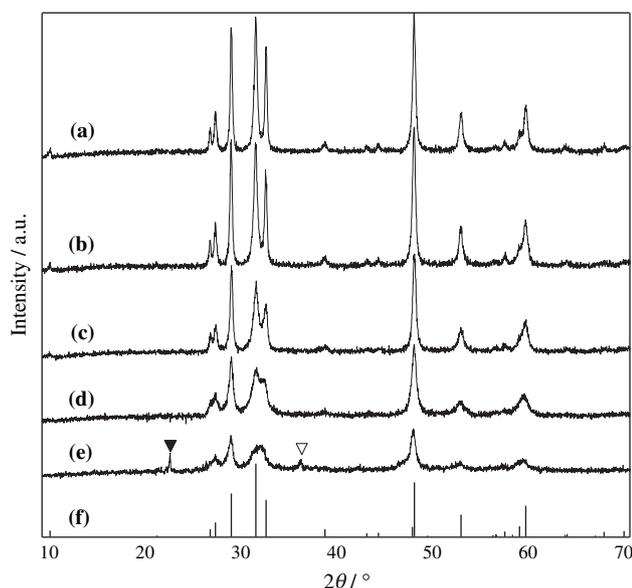


Fig. 2. The XRD patterns of the CuS products obtained at (a) $180 \text{ }^\circ\text{C}$ for 60 h, (b) $180 \text{ }^\circ\text{C}$ for 10 h, (c) $120 \text{ }^\circ\text{C}$ for 10 h, (d) $60 \text{ }^\circ\text{C}$ for 10 h, and (e) $60 \text{ }^\circ\text{C}$ for 1 h. (f) Reported pattern of CuS (JCPDS Card No. 06-0464). Open inverted triangle and filled inverted triangle show the main peaks of Cu_2O (JCPDS Card No. 05-0667) and S (JCPDS Card No. 08-0247), respectively.

phase reaction between copper and sulfur, allowing the complete reaction to occur. As mentioned previously, elemental copper and sulfur react to form CuS at near ambient temperatures (reaction starts at $\sim 46 \text{ }^\circ\text{C}$) [5]. However, the reaction is restricted to the surface of the particles. The formation of surface CuS layers on the copper reactant limits interdiffusion of the copper and sulfur reactants, thus passivating the surface. Indeed, Blachnik and Muller observed that copper and sulfur samples subjected to reaction at low temperatures consist of deep blue black spheres (CuS) with a core of copper metal [5]. Higher temperatures ($>165 \text{ }^\circ\text{C}$) are required to enhance diffusion and yield phase-pure CuS in the solid-state reaction. In water, however, the solid-state reaction proceeds to completion at much lower temperatures ($60 \text{ }^\circ\text{C}$ for 10 h). Here water provides a medium to continuously transport solid sulfur (m.p. $\sim 120 \text{ }^\circ\text{C}$) to the reactant copper surface, thereby avoiding passivation and completing the solid-state reaction at low temperatures. This passivity prevention and breakdown mechanism is common in metal–sulfur–water systems, and has been studied extensively by corrosion scientists [22].

As mentioned previously, the addition of water to the reaction between elemental copper and sulfur enables a corrosion reaction to occur. From a corrosion perspective, however, sulfur induces the enhanced corrosion/reaction of metals in contact with aqueous solutions. Sulfur increases metal corrosion in aqueous environment by (1) preventing the formation of a passivating metal oxide layer, and (2) disrupting any passivating layer that forms on the metal surface. First, adsorbed sulfur inhibits metal oxide passivation, and therefore has been studied extensively owing to its importance in the areas of corrosion and electrocatalysis [23,24]. Adsorbed sulfur limits the sites of adsorption for hydroxyl ions, which are required precursors in the formation of a metal oxide passive layer. Indeed, there is a competition between the adsorption of oxygen and sulfur species on the metal surface [25]. The adsorption of oxygen, in the form of hydroxyl groups, or sulfur species onto copper surfaces in aqueous solutions leads to the formation of a Cu_2O or CuS layer, respectively. If the elemental copper surface is replenished consistently, over time the copper metal will corrode, generating significant amounts of either of the above product or both. If not, a passivating layer of Cu_2O forms over the reactive copper surface and prevents further corrosion.

In the present experiments, sulfur was shown to react with copper at $60 \text{ }^\circ\text{C}$ for 1 h to generate CuS as the major product, with trace amounts of Cu_2O , Cu, and S as alternate phases. The presence of Cu_2O in the product confirms that there is initial competition on the copper surface for adsorption of oxygen and sulfur. Cu_2O is eliminated from the reaction products by either removing oxygen from the pressure vessel or by increasing reaction times. Oxygen-free experiments were conducted at $60 \text{ }^\circ\text{C}$ for 1 h by sealing the pressure vessel in an argon atmosphere and using oxygen-free water. As expected, the removal of oxygen from the reaction results in no XRD-detectable Cu_2O in the products. There is, however, unreacted Cu and S present in addition to CuS after 1 h. This indicates that longer reaction times are required to complete

the reaction, and, indeed, phase-pure CuS is obtained when the reaction time is extended to 10 h at 60 °C. Note that even in the presence of oxygen, Cu₂O is not formed in the reaction at 60 °C for 10 h. This is because sulfur in an aqueous reaction system not only limits the formation of a passivating oxide film, but over time induces passivity breakdown of copper oxide surface layers [22]. After the passive Cu₂O film is broken down, the presence of sulfur on the surface also hinders repassivation by Cu₂O. Instead, copper metal is oxidized in the presence of sulfur, covering the surface with CuS.

Similar to the solid-state reaction, in water elemental copper and sulfur undergo reaction to form CuS at near ambient temperatures on the surface of the copper metal. Unlike the solid-state reaction, however, passivation by the CuS product that forms on the surface of the copper reactant is not problematic in the presence of water. In the presence of water, sulfur adsorbs onto the copper metal surface, and continues to accumulate until a threshold coverage is attained, which is of the order of one monolayer [22]. Above this threshold coverage, disruption of the adsorbed sulfur film occurs, precipitating CuS. The time to initiate the passivity breakdown decreases with increasing sulfur content [21], which is high in the present reactions since sulfur is a reactant. After the CuS film ruptures, a thin layer of copper sulfide remains. This thin CuS layer is not protective, and CuS continues to form in a reaction between copper and sulfur on the now pitted copper surface. Over time, the process repeats until all reactants are consumed since the reaction is not limited by solid-state diffusion at low temperatures. Therefore, addition of water to the solid-phase reaction between copper and sulfur constantly exposes a fresh copper surface to react with elemental sulfur and form CuS at temperatures as low as 60 °C.

The size and shape of the as-prepared CuS particles were investigated by scanning electron microscopy (SEM). SEM images of the product produced at 180 °C over 10 h reaction time in air are shown in Fig. 3. Micrometer-sized polyhedral particles with dimensions of 2–3 μm are formed as shown in Fig. 3(a). Furthermore, a secondary structure is observed, as shown in Fig. 3(b), with the particles aggregating to form layers.

5. Conclusions

Polycrystalline CuS was prepared by the reaction between elemental copper and sulfur at low temperatures (≥ 60 °C) in water. In the presence of water, sulfur prevents the formation of an oxide passivating layer and disrupts the CuS passive film to constantly expose the reactant copper surface, thereby allowing the formation of CuS to proceed at low temperatures. While this basic corrosion process can be economically detrimental, it proves beneficial for the synthesis of CuS at low temperatures. These results underscore the utility of the corrosion science literature in improving the understanding and synthetic utility of preparative reactions in contact with water.

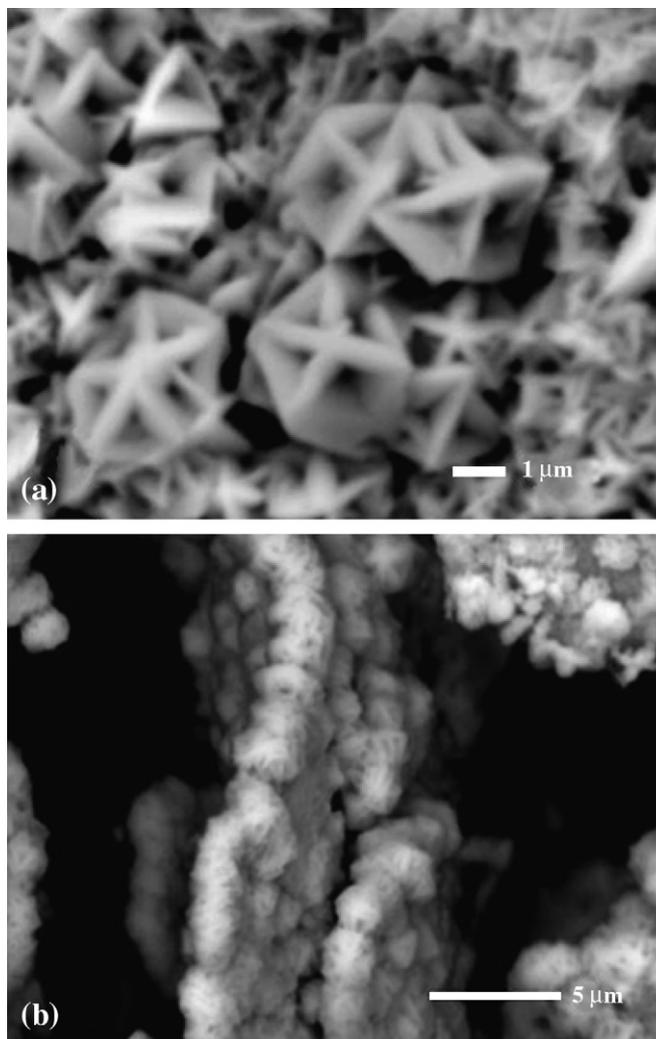


Fig. 3. The SEM images of CuS products obtained at 180 °C for 10 h: (a) 2–3 μm polyhedral microcrystals and (b) layer-structures consisting of these particles.

Acknowledgments

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