Preparation and Characterization of CuS Nanoparticles Prepared by Two-Phase Colloidal Method

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Abstract: In this paper, two-phase colloidal method was employed to synthesis CuS nanoparticles with different Cu : S ratios. The characterization of prepared CuS involves structural, morphological and optical properties analysis. X-Ray Diffractometer indicate that the covellite CuS have hexagonal structure. Field Emission Scanning Electron Microscope showed the formation of spherical nanostructure of CuS. UV-Visible Spectrophotometer showed the two absorption peaks of CuS nanoparticles one at UV-Visible region and the second at near infra-red region and the energy gap increase with sulfur content.

Keywords: CuS nanoparticles, UV-VIS, FESEM, Cu : S ratios, optical properties.

1. Introduction

Recently, nanomaterials have attracted a large attention due to their unique properties. In the 1960s and 1970s copper sulfide (Cu₂S) was still a widely studied material concerning solar cells [1]. CuS have wide range of applications such as energy conversion and storage [2], optoelectronic devices [3], gas sensors and solar cells [4], etc. due to their structural, optical and electrical properties [5]. CuS is an abundant material with several phases that’s have various stoichiometries from covellite (x = 1) to chalcocite (x = 2) and have band gaps range between 1.3 and 2.4 eV [6-8]. The CuS plasmonic activity attracts special attention [9-15]. It typically occurs from the nonstochiometric nature with a copper deficiency that leads to partial filling of 3p orbitals of sulfur, and this causes the vacancies generation [16]. The vacancies lead to creating free holes that’s makes the pure, self-doped CuS excellent electrical conductive. The amount of charge carriers increases, when the amount of copper decreases in the compound reaching large concentrations of carriers about 10²⁰-10²¹ cm⁻³ [12]. The covellite CuS have special properties such as large concentration of holes reaching 10²² cm⁻³ [11] depending on the specific structure. The covellite phase of CuS has a distinct anisotropic metallic conductivity [17] and inherent high degree of hole delocalization [18]. CuS demonstrates a highly absorption peak of localized surface plasmon resonant (LSPR) in the NIR region [19]. Control of the oscillator strength, the position and width of the LSPR peak depends on the shape, size and the nanostructure surface chemistry adjustment [20]. There are various morphology of CuS such as nanorods, nanodisks, nanoflowers, hollow sphere and nanowires was found. This paper focuses on the effect of Cu : S ratio on the properties of copper sulfide (covellite) prepared by two-phase colloidal synthesis method.
2. Synthesis of CuS nanoparticles

Two-phase colloidal synthesis method was used to prepare copper sulfide nanoparticles. Sulfur solution (0.15 M) was synthesized by using oleylamine (C_{18}H_{35}NH_{2})/1-octadecene (C_{18}H_{36}) mixture solution (4 mL, 1:3 volume ratio) to dissolve 0.0192 g of sulfur powder in a glass vial. The solution became orange after 5 min of ultrasonication. Water/1,5-pentanediol (C_{5}H_{12}O_{2}) mixture solution (4 mL, volume ratio of 1:6) was used to dissolve 0.0966 g of copper nitrate (Cu(NO_{3})_{2}.3H_{2}O) and 0.2 mmol KI to prepare 0.1 M of (Cu(NO_{3})_{2}.3H_{2}O with 0.1 mmol I^{-} solution. The addition of the last solution to the sulfur solution, lead to formation of bottom layer of hydrophilic Cu(NO_{3})_{2}.3H_{2}O solution and top hydrophobic layer of sulfur solution. The reaction vial was surrounded by the oil bath at 180 °C for 30 min. The color of sulfur solution converted from orange to a dark green-blue. After cooling to room temperature, 4 mL of ethanol (C_{2}H_{5}OH) was added. The free oleylamine and 1-octadecene were removed by centrifugation (3000 rpm for 5 min) of solution. To remove any byproducts, the powder was dispersed using chloroform acid (CHCl_{3}) and placed in centrifuge (7500 rpm for 7.5 min). The resultant powder have a ratio Cu:S = 1:1.5. To study the effect of Cu : S ratio on CuS properties, different ratios Cu : S = 1:2 and 1:2.5 were prepared by using different sulfur concentrations 0.20 and 0.25 M respectively.

3. Material characterization

After preparing copper sulfide samples, the CuS phases and crystalline structure were demonstrated using X-Ray Diffractometer (Philips PW1730). Mira 3-XMU Field Emission Scanning Electron Microscope was used to characterize the morphology of nanoparticles. The absorption and optical band gap of synthesized copper sulfide were investigated by using T80+ UV/VIS spectrophotometer (PG Instruments Ltd) at 400 – 1100 nm wavelength range.

4. The results and discussion

The X-Ray diffraction of the copper sulfide structures fabricated by two-phase colloidal synthesis method at 180 °C with different Cu : S ratio (1:1.5, 1:2 and 1:2.5) are shown in Figure 1. Covellite CuS with hexagonal structure indexed in (103), (110), (108) and (116). These results agree with that’s of the covellite hexagonal copper sulfide JCPDS card no. 01-078-0877 and have good agreement with previous studies [20,21,22]. The other phases of CuS or impurities peaks were not appeared, that’s referring to the complete reaction between the precursors and CuS nanostructure was produced. Scherrer formula was used to calculate the crystallite size of covellite copper sulfide [23,24,25]:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \), \( \theta \) and \( \beta \) are the wavelength of X-Ray (1.54 A\(^{\circ}\)), diffraction angle and full width at half maximum of diffraction peak (FWHM) respectively. The constant \( k \) take the value (0.89 < \( k \) < 1). The obtained crystallite sizes are 12.29, 16.37 and 24.58 nm for copper sulfide prepared with ratios Cu : S = 1:1.5, 1.2, 1.2.5 respectively. Table 1 shows the angle 20 values and crystallite size of CuS nanoparticles.
Figure 1. XRD pattern of CuS that’s prepared with different Cu : S ratios

| Sample          | Angle 2θ° | Crystallite size (nm) |
|-----------------|-----------|-----------------------|
| JCPDS 01-078-0877 | 31.78, 47.91, 52.72, 59.32 | |
| Cu : S = 1:15    | 31.84, 47.91, 52.65, 59.18 | 12.29 |
| Cu : S = 1:2     | 32.01, 48.06, 53.02, 59.39 | 16.37 |
| Cu : S = 1:2.5   | 31.53, 47.92, 52.80, 59.27 | 24.58 |

Table 1: The angle 2θ values and crystallite size of CuS nanoparticles.

It can be observed that the copper sulfide crystallite size increased when S content increased, that’s shown in Figure 2, because the increasing of S content promotes the growth and formation of nanoparticles. This refers to that there are two factors influence on CuS nanoparticles formation: one; Cu and S reactivity balancing (synthesis under sulfur excess) and the second; growth kinetic mode [20].

Figure 2. The change of crystallite size with sulfur content
The copper sulfide morphology was characterized by FESEM and shown in Figure 3. The aggregation of nanoparticles was clear in FESEM images. It can be seen from the images, the samples have been formed with sphere-like structures. This images exhibited that when the Cu : S ratio changed, different average diameters of nanostructures was obtained. The obtained average diameters are 23, 29.08 and 24.08 nm for Cu : S = 1:1.5, 1:2, 1:2.5 respectively.

To investigate the optical properties, CuS nanoparticles were dispersed in carbon tetrachloride to give an isotropic suspension. Figure 4 shows the optical absorption spectra for the CuS nanoparticles prepared with different Cu : S ratios. The absorption peaks in UV-VIS region appeared at 518, 474 and 442 nm for Cu : S = 1:1.5, 1:2 and 1:2.5 ratios respectively which was attributed to excitonic transitions across a direct band gap and hardly depends on the CuS particles size [11,20]. Localized surface plasmon resonance (LSPR) in NIR range is a distinct spectral property that’s influenced by the changes of shape and size. In NIR region, broad peaks of CuS were appeared at 970, 1032 and 1049 nm for Cu : S = 1:1.5, 1:2 and 1:2.5 ratios respectively, that’s related to LSPR of CuS. The broadening of (LSPR) spectra can be attributed to overlap occurs between the spectra of two modes of localized surface plasmon resonance associated with two different sizes nanocrystals [26]. The absorption peaks in NIR region have red shift to
longer wavelength when the sulfur content increased that’s attributed to the morphology and size of different CuS products [27].

![Figure 4](image-url)

**Figure 4.** The absorption spectra of CuS that’s prepared with different Cu : S ratios

The band gap of CuS was obtained using eq. 2, with the absorption spectra [28,29,30].

\[(\alpha h\nu)^n = A(h\nu - E_g) \quad \ldots \ldots (2)\]

The energy gap was determined by the plot of \((\alpha h\nu)^n\) on y-axis vs. \((h\nu)\) on x-axis, where \(h\nu\), \(\alpha\), \(E_g\) and \(A\) are the photon energy, absorption coefficient, band gap and constant respectively. The constant \(n\) is take the value \(\frac{1}{2}\) or 2 for indirect or direct transition respectively. The band gap was given by the straight line intercept on the x-axis (energy axis) in the plot [31,32,33]. Figure 5 shows the optical \(E_g\) of CuS nanoparticles. The direct optical \(E_g\) values were obtained as 1.96, 2.14 and 2.26 eV for \(Cu : S = 1:1.5\), \(1:2\) and \(1:2.5\) ratios respectively. This results have good agreement with other studies [34,35]. Figure 6 shows the relation between the energy gap of CuS and the Cu : S ratios. From this figure we can observe that the energy gap increased when sulfur content increased. In this case the increasing of crystallite size (crystallite size that’s obtained by XRD) with S content may be lead to decrease the packing of the atoms to each other and the interatomic spacing increase that’s lead to higher band gap.
Figure 5 The optical energy gap of CuS that’s synthesized with different Cu : S ratios

Figure 6. Relation between the energy gap of CuS and sulfur content
5. Conclusion

Briefly, CuS was prepared by using two-phase colloidal synthesis method with three different Cu : S ratios (1:1.5, 1:2, and 1:2.5). The XRD pattern showed that covellite copper sulfide nanoparticles have hexagonal structure. Covellite in nanosized is a promising material for biomedical applications such as bioimaging, NIR chemo-photothermal therapy and biosensing because it exhibits plasmon absorption range in the near IR where biological tissues weakly absorb. UV-VIS results conforms that and shows the broad peaks at NIR range 970-1049 nm which are typical of a LSPR spectrum of CuS. FESEM demonstrated that the spherical nanostructure of CuS was obtained with aggregation of nanoparticles.

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