Study the Structural, Morphological and Optical Properties of Copper Sulfide Prepared by Two-Phase Colloidal Method

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Abstract: In this paper, copper sulfide nanoparticles were synthesized by two-phase colloidal method with different reaction temperatures (140, 160, 180 and 200°C). The structural, morphological and optical properties of prepared CuS were analyzed by the X-Ray Diffractometer (XRD), Field Emission Scanning Electron Microscope (FESEM) and UV-VIS Spectrophotometer. The XRD peaks refer to the covellite copper sulfide with hexagonal structure. FESEM showed the rod formation at lower temperatures (140 and 160°C), whereas higher temperatures (180 and 200°C) form nanocrystals within spheres structures. UV-VIS showed that CuS nanoparticles have two absorption peaks, one at UV-VIS region and the second at NIR region and its energy gap decrease with increasing of reaction temperature.

Keywords: CuS nanoparticles, UV-VIS, FESEM, reaction temperatures, Localized Surface Plasmon Resonance

1. Introduction

In the recent few years metal sulfide nanomaterials have attracted attention due to the favored electronic and optical properties that’s result from the size in the nanometer scale. The quantum size effects lead to large difference in the nanoparticles properties as compared with those of bulk materials and this make them attractive for applications such as solar cells [1], drug delivery [2], light emitting diodes [3], fuel cells [4] and as catalysts for industrial transformations [5]. Most metal sulfide semiconductor studies are focused on chalcogenides (group 12) especially zinc sulfide [6,7] and cadmium sulfide [8,9] but these materials toxicity lead to limiting applications. This limitation makes copper sulfide nanocrystals have gained interest in various applications in recent years. Furthermore CuS has various stoichiometric compositions with several phases [10]. At room temperature copper sulfides have different phases involving: (CuS) covellite, (Cu1.8S) digenite, (Cu1.95S) djurleite and (Cu2S) chalcocite. Copper sulfide has various morphologies such as nanorods, hollow sphere, nanowires, nanoflowers, nanoplatelets, nanoflakes, nanotubes and nanodisks. The semimetallic behavior and high carrier concentration of copper sulphide (covellite) makes it one of the most promising chalcogenides for localized surface plasmon resonance (LSPR) excitation. NIR chemo-photothermal therapy, biosensing

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and bioimaging applications were based on CuS due to its LSPR peak located at the NIR region [11]. Copper sulfide morphology and stoichiometry, along with the method of obtaining nanoparticles have effect on the position and intensity of the surface plasmon resonance peak. The preparation methods of copper sulfide have been reported including thermolysis, template-assisted growth, microwave irradiation, electrodeposition, hydrothermal or solvothermal and chemical vapor reaction [12, 13, 14, 15, 16]. In this paper, copper sulfide (covellite) nanoparticles was prepared by two-phase colloidal synthesis method and the reaction temperature effect on the properties of that’s was reported.

2. Synthesis of CuS nanoparticles

Copper sulfide nanoparticles prepared by two-phase colloidal synthesis method. 0.0192 g sulfur powder was dissolved in a 4 mL of oleylamine (C_{18}H_{35}NH_{2})/1-octadecene (C_{18}H_{36}) mixture solution (volume ratio of 1:3) in a glass vial to prepare 0.15 M sulfur solution. The solution was ultrasonicated for 5 min that’s lead to formation of orange solution. 0.0966 g copper nitrate (Cu(NO_{3})_{2}.3H_{2}O and 0.2 mmol KI were dissolved in a 4 mL of water/1,5-pentanediol (C_{5}H_{12}O_{2}) mixture solution (volume ratio of 1:6) to prepare 0.1 M copper nitrate with 0.1 mmol I\(^{-}\) solution. (Cu(NO_{3})_{2}.3H_{2}O solution was added to the sulfur solution, that’s lead to formation of solution with the copper nitrate hydrophilic solution as the bottom layer and sulfur hydrophobic solution as the top layer. The glass vial was embedded in an oil bath at 140 °C for 30 min. The orange color of sulfur solution converted to a dark green-blue. After cooling to room temperature, 4 mL of ethanol (C_{2}H_{5}OH) was added. To remove free oleylamine and 1-octadecene, solution was centrifuged at 3000 rpm for 5 min. To remove any byproducts, the powder was dispersed using chloroform acid (CHCl_{3}) and placed in centrifuge (7500 rpm for 7.5 min). To study the temperature effect on the prepared CuS, different temperatures (160, 180 and 200°C) were used.

3. Material characterization

After preparing CuS samples, the X-Ray Diffractometer (Philips PW1730) was used for determination of phases and crystalline structure of CuS. For characterization of prepared nanoparticles morphology, Field Emission Scanning Electron Microscope (Mira 3-XMU) was done. The optical analysis was done by using T80+ UV/VIS spectrophotometer (PG Instruments Ltd) at the wavelength 400nm – 1100 nm to show the optical absorption peaks of the CuS nanoparticles.

4. The results and discussion

The XRD pattern of the prepared CuS powder with reaction temperatures 140, 160, 180 and 200°C was shown in Figure 1. Various reaction temperatures refer to the formation of crystalline CuS. The XRD shows that all of the peaks refer to covellite copper sulfide and indexed as [103], [110] and [116] of the CuS with hexagonal structure. These results agree with those of the hexagonal CuS (covellite) JCPDS card no. 01-078-0877. The peaks of impurities or other CuS phases were not found, that’s confirm the completely reaction of the precursors and CuS nanostructure was produced. The crystallite sizes of covellite CuS are calculated by Scherrer formula [17,18]:

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

Where λ, θ and β are the X-Ray wave length (1.54 Å), diffraction angle and diffraction peak full width at half maximum (FWHM) respectively. The constant k take the value (0.89 < k < 1). The obtained values
of crystallite size are 14.74, 21.04, 12.29 and 12.27 nm for CuS prepared at 140, 160, 180 and 200 °C respectively.

![XRD patterns of CuS samples prepared with different reaction temperatures](image)

Figure 1: XRD patterns of CuS samples were prepared with a different reaction temperatures.

The CuS nanostructures morphology were characterized by FESEM and shown in Figure 2. FESEM images exhibited that when the reaction temperatures changed, different morphology of nanostructures was obtained. The FESEM image for each sample shows that the nanoparticles aggregate to each other and the obtained average diameters are 33.7, 42.3, 23 and 29.3 nm for 140, 160, 180 and 200 °C respectively. At 140 °C, it can be seen from the image, the samples have been formed with rod-like structures, also, there are some nanospheres presented in the products. At 160 °C the nanorod structures becomes very clear. Reaction temperatures 180 and 200 °C greater isotropic spherical growth. FESEM of prepared CuS shows that spheres and rods form simultaneously in this system. Rod formation was favored at lower temperature, whereas at higher temperatures spherical nanocrystals crystallization kinetics was produced that’s become isotropic and overcome the energetic barrier that’s favor asymmetric growth of nanorod. These results have good agreement with previous study [19].
Figure 2: FESEM of CuS samples were prepared with a different reaction temperatures.

The absorbance spectra of CuS nanoparticles were recorded by disperses CuS nanoparticles in carbon tetrachloride to give an isotropic suspension. The optical absorption peaks of the CuS nanoparticles prepared with various reaction temperatures was shown in Figure 3. In UV-VIS range, the absorption peaks appeared at 481, 478, 518 and 473 nm for 140, 160, 180 and 200 °C respectively which was related to excitonic transitions across a direct band gap and hardly depends on the size of particles [14,20]. Localized Surface Plasmon resonance is a distinct spectral feature appears at the NIR region that’s affected by the changes of size and shape. The NIR spectra shows broad peaks at 929-1020, 944-1025, 920-1021 and 992-1000 nm for CuS nanoparticles prepared at 140, 160, 180 and 200 °C respectively, which are typical of LSPR spectrum of CuS. There are small differences in absorption peaks of samples were attributed to the morphology and size of different CuS products [21]. 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 [11].
CuS band gap was obtained using eq. 2, with the absorption spectra [22,23].

\[(\alpha h\nu)^n = A(h\nu - E_g)\]  \hspace{1cm} (2)

To find the energy gap, the plot of \((\alpha h\nu)^2\) vs. \((h\nu)\) was done, where \(h\nu\) is the photon energy, \(\alpha\) is the absorption coefficient, \(E_g\) is the band gap, \(A\) is a constant and \(n\) is take the value \(\frac{1}{2}\) or 2 for indirect or direct transition respectively. The intercept of the straight line on the energy axis in plot of \((\alpha h\nu)^2\) vs. \((h\nu)\) gives the energy band gap [24]. Figure 4 shows the optical band gap of CuS nanoparticles. The direct optical band gap values were obtained as 2.06, 2.1, 1.96 and 2.14 eV for CuS prepared at 140, 160, 180 and 200 °C respectively. This result has good agreement with other studies [25,26]. Figure 5 shows the relation between the energy gap of CuS and the reaction temperature. From this figure we can observe that the energy gap increased with increasing of reaction temperature that’s attributed to changing of crystallite size of samples that was calculated from Scherrer formula. The CuS nanoparticles that are prepared at 180 °C have energy gap value 1.96 eV lower than that of other temperatures. In this case the nano crystallite size (crystallite size that was obtained from XRD) may lead to packing of the atoms to each other (The packing of the atoms is clear in FESEM image) and the interatomic spacing decrease that’s lead to lowering band gap.
Figure 4: The optical energy gap of CuS samples were synthesized at various reaction temperatures.

Figure 5: The relation between the energy gap of CuS and the reaction temperature.

5. Conclusion

In summary, two-phase colloidal synthesis method with different reaction temperatures (140, 160, 180 and 200°C) was employed to prepare the CuS nanoparticles. The XRD pattern indicates to the covellite copper sulfide with hexagonal structure. FESEM images demonstrated that the rod formation was favored at lower temperature, while at higher temperatures spherical shapes were produced. UV-VIS spectrophotometer gives the fundamental absorption in UV-VIS region lower than 600 nm that’s
depended on the particles size and gives the energy gap values 1.96 - 2.14 eV. The NIR spectra shows broad peaks at range 920-1025 nm which are typical of a LSPR spectrum.

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