Synthesis and Characterization of CuS/PVA Nanocomposite via Chemical method

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Abstract: Nanocomposite of copper sulfide (CuS/PVA) have been synthesized according to chemical precipitation method at temperature 65°C by simple reaction between copper acetate (Cu (ac)) and thiourea (H2NCSNH2) at pH=9. Polyvinyl Alcohol (PVA), used as capping agent, was found to play a key role in the confinement process.

The characterization of the product was done by UV-VIS spectroscopy, atomic force microscopy (AFM) and x-ray diffraction (XRD). The X-ray diffraction showed the covellite phase of copper sulphides with hexagonal crystal structure. The sizes of the sample as prepared were calculated by Debye-Scherrer formula according to XRD spectra. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanocomposite CuS to be about 3.3 eV.

Keywords: Nanocomposite; Atomic Force Microscopy; Polyvinyl Alcohol.

I. Introduction

Copper sulphides belonging to the I-IV compound semiconductor material [1,2] and are among the chalcogenides compounds with several application in Nanosciences. They are found very useful in coating solar energy conversion systems and solar controlled devices. The chalcogenides are also used in the fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor applications [2]. Moreover, ternary copper halogenides like copper indium diselenide and copper indium gallium selenides, in recent times, are now widely used in the fabrication of solar photovoltaic cells [3]. Special attention is given to the study of copper sulphide thin films due to the discovery of the CdS/CuxS heterojunction solar cell [2]. Synthesis and characterization of nanocrystals of semiconducting metal sulphides have been an intense field of research due to their interesting properties and potential applications [4-5].

Copper sulphide has fairly complex crystal chemistry owing to its ability to form sub- stoichiometric compounds CuxS (2≥x≥1) [6]. CuS phase exists in two forms, the amorphous brown chalcocite CuS and green crystalline covellite [7]. CuS has many forms in bulk at room temperature. They are chalcocite (orthorhombic Cu2S), djurleite (mono-clinic-prismatic Cu1.95S) etc. [8, 9]. In the chalcocite group, Cu2-xS (0≤x≤0.6), eight compounds exist. They are σ-chalcocite Cu2S (low, orthorhombic), β-chalcocite Cu2S (high, hexagonal), djurleite Cu 1.77S, digenite Cu1.80S, roxbyite Cu 1.78S, anilite Cu 1.75S, greerite Cu 1.60S and spionkopite Cu 1.60S. While γ-chalcocite, djurleite and anilite form low temperature phases, the tetragonal Cu 1.96S phase, low digenite, Cu 1.8S and roxbyte, Cu 1.75S form metastable phases [10].

II. Experimental

CuS nanoparticles were prepared by reacting copper acetate Cu (ac) with thiourea (H2NCSNH2) in the presence of polyvinyl alcohol (PVA) as capping agents. A 3% PVA solution was mixed with copper acetate solution to act as capping agent. Equivolume and eqimolar (0.01M) solution of copper acetate and thiourea were used for the synthesis. Ammonia was added to the PVA mixed copper acetate solution to make copper ion complex and the pH was kept at 9. Then thiourea solution was added drop wise for the formation of final copper sulphide matrix solution. The synthesized copper sulphide solution became greenish in color.

X-ray diffraction was recorded with an automated X'pert Philips diffractometer with Cu Ka radiation beam λ=1.5406 Å. The optical absorption measurements obtained from the colloidal solution were performed in UV-Vis spectrophotometer SP-3000 plus, OPTIMA INC. Japan. In order to investigate the surface morphology and surface roughness, the atomic force microscopy (AFM) observations were performed using an SPM model AA 3000, Angstrom Advanced Ins.v ,USA. The AFM images were analyzed with the Pro Scan software, calculating the root mean square surface roughness value.

III. Result and Discussion

1 XRD studies

The crystalline nature of the prepared nanocomposite CuS is evident from the x-ray diffraction pattern Figure (1). The most significant feature within the observed pattern, at 2θ=21.10997, is assigned to the (004) reflection of the hexagonal primitive covellite CuS crystal structure as observed by ICSD # 041975 card no. 78-
Two other prominent features are observed at 2θ = 31.8761 and 34.0253, which belong to (103) and (104) reflections.

From the x-ray patterns the broadening of the diffraction peaks of the nanocomposite is obvious which is characteristic of grain size by applying Debye- Scherrer formula

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)

Where D is the mean crystallite size, \( \lambda \) is the wavelength of incident X-ray (1.5406 Å), \( \theta \) is the degree of the diffraction peak, and \( \beta \) is the full width at half maximum (FWHM) of the XRD peak appearing at the diffraction angle \( \theta \). The grain size of the CuS nanocomposite shows that the synthesized nanocomposite is in the quantum confinement regime as shown table (1).

The calculations done in (Table 1) are done by following formulas:

Average strain by stokes Wilson equation:

\[ \varepsilon_{\text{strain}} = \frac{\beta}{4 \tan \theta} \]  \hspace{1cm} (2)

Dislocation density (lines nm\(^{-2}\))

\[ \delta = \frac{1}{D^2} \]  \hspace{1cm} (3)

d-Spacing by Bragg’s equation

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (4)

<table>
<thead>
<tr>
<th>hkl</th>
<th>2θ</th>
<th>( \beta \times 10^{-3} )</th>
<th>Grain size (nm)</th>
<th>( \varepsilon_{\text{strain}} \times 10^{-3} )</th>
<th>( \delta \times 10^{-3} ) (nm(^{-2}))</th>
<th>d-Spacing, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>004</td>
<td>21.1097</td>
<td>21.711</td>
<td>21.4</td>
<td>6.6</td>
<td>28.72</td>
<td>22.95</td>
</tr>
<tr>
<td>103</td>
<td>31.8761</td>
<td>31.756</td>
<td>5.75</td>
<td>25.04</td>
<td>5.03</td>
<td>1.59</td>
</tr>
<tr>
<td>104</td>
<td>34.0253</td>
<td>34.989</td>
<td>5.7</td>
<td>25.4</td>
<td>4.67</td>
<td>1.55</td>
</tr>
</tbody>
</table>

2. AFM Studies

Atomic force microscopy (AFM) is an excellent tool to study morphology and texture of diverse surfaces. The knowledge of the surface topography at nanometric resolution made possible to probe surfaces. The versatility of this technique allows meticulous observations and evaluations of the textural and morphological characteristics of the sample, showing better facilities than other microscopic methods. AFM scanned the surface in 3D and the analysis of the images allow the determination of the average height of the particles, the root mean square roughness and the power spectra density gives the periodicity in the arrangement of particles [11]. Using adequate software, it is possible to evaluate characteristics such as roughness, porosity, average size, and particle size distribution, which influence directly the optical, mechanical, surface, magnetic and electrical properties of sample. The Figure (2) corresponds to the surface morphology of CuS nanocomposite.

The Atomic Force Microscopy images gave us information about the representative surface morphology and roughness for the case of the CuS. From the images we can have information that other than spherical crystal shows nanocomposite formation.
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The Root Mean Square (RMS) roughness which is defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness [12]. The RMS roughness calculates the standard deviation of the surface irregularities with respect to some mean line or curve. It is commonly used to characterize optical components, in general the lower the RMS value, the less light is scattered by an optical surface, and hence the better the surface quality [13]. This parameter is used when the distribution of surface irregularities is random. Its value depends on the sampling length. The root-mean square (RMS) roughness of CuS nanocomposite is 2.52 nm. The Roughness average of CuS nanocomposite is 2.15 nm. The average diameter for CuS was 95.80 nm.

3. Optical Properties:
Optical transmittance spectra of CuS nanocomposite in the range of (300-800) nm was presented in Figure (3), measured at room temperature in air. The results indicate that T increases with the increasing of the incident wavelength $\lambda$.

![Optical transmittance spectra of CuS nanocomposite](image)

**Fig. 3:** Optical transmittance spectra of CuS nanocomposite

Figure (4) shows the absorbance spectra of CUS nanocomposite. It was clearly seen that the absorbance decreases with increasing the wavelength. The sharp increase in absorbance at the wavelength $\lambda= 365$ nm is due to the onset of interband transitions at the fundamental edge.
The band gap values were determined from the intercept of the straight-line portion of the $(\alpha h\nu)^2$ against the $h\nu$ graph on the $h\nu$-axis using a computer fitting program Figure (5).

The linear part shows that the mode of transition in these films is of direct nature. The calculated band-gap value of the CuS nanocomposite is $\sim 3.3$ eV. This result is in agreement with this of other study. [14]

![Figure 4: The variation of the absorbance with wavelength for CuS nanocomposite](image)

IV. Conclusion

The copper sulfide nanocomposite can be prepared through simple chemical route. The XRD confirms the formation of copper sulphides showing the diffraction peaks of the corresponding materials. Copper sulphides exhibit covellite. The mean calculated grain size of the CuS nanocomposite is 19 nm. AFM image is used to study the morphology of the synthesized nanocomposite.

The formation of nanocomposite was confirmed by using UV-visible absorption measurements. The absorption spectra exhibit the peaks in the range 365 nm which are expected owing to the existence of the covellite phase. The energy gap for the synthesized CuS nanocomposite is 3.3 eV.

Reference


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