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Microstructural and optical properties of CuS nanoparticles prepared by sol—gel route☆

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Summary This paper demonstrates the synthesis of CuS nanoparticles using sol—gel route in the presence of distilled water at 100 °C for 3 h. X-ray diffraction (XRD), energy dispersive X-ray spectrum (EDS), and scanning electron microscope (SEM) techniques were employed to study the microstructural properties of the prepared sample. Crystallite size was determined by Debye—Scherrer formula and was found to be 17.73 nm. The EDS spectrum shows a clear peak of Cu and S elements. SEM images show the morphology of the CuS nanostructures. Optical analyses were done by UV—visible and Fourier Transform Infra-Red Spectroscopy (FTIR) techniques. The band gap was calculated by Tauc relation and came out to be 2.89 eV.

Introduction

Copper sulphides with the formula Cu_xS_y describe a family of chemical compounds and minerals. Some copper sulphides are economically important ores. Naturally, it occurs as the dark indigo blue mineral covellite. Copper sulphide serve as an important base material as absorber coating and is extensively used in photovoltaic and photodetectors applications due to its unique near solar control characteristics (Khiew et al., 2004). It is also a moderate conductor of electricity (Blachnik and Müller, 2000) and has its potential use in catalysis (Kundu and Pradhan, 2014). The chemical, physical and toxicological properties of copper sulphide have not been thoroughly investigated and recorded. In order to investigate various properties of the prepared sample, it has to go under a number of characterization techniques. Doping is an effective method to moderate the properties of nanomaterial's (Agrawal et al., 2015, 2016). In this paper we have successfully synthesized CuS nanoparticles using sol—gel route and investigated various structural and optical properties (Figs. 1 and 2).

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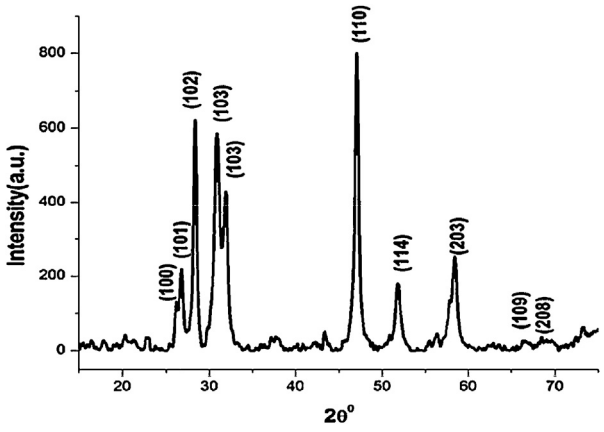

Figure 1 (a) XRD pattern of CuS NPs.

Experimental details

Copper nitrate $Cu(NO_3)_2$ and sodium sulphide (Na_2S) have been taken as the precursor material for the preparation of CuS nanoparticles 9.38 g of the $Cu(NO_3)_2$ is taken and 0.5 M solution is made by dissolving it into 100 ml of distilled water. The solution is then subjected to stirring at 100—150 rpm at room temperature. The next step in the synthesis is the gelation. This is achieved by mixing the sodium sulphide in the copper nitrate sol. 0.5 M solution of sodium sulphide (Na_2S) is made in 50 ml distilled water by dissolving the 1.95 g of Na_2S. The mixture was stirred at 450—500 rpm at room temperature. After the constant stirring for 10—15 min, the mixture was converted into a gel and this gel was then kept undisturbed for 2—3 h for precipitation. The precipitate was then centrifuged two or three times at 4500 rpm for 5 min and washed. This precipitate was further dried in the vacuum oven at 100 °C for 2—3 h. The dried precipitate was then ground and the powder was kept for further characterizations.

Results and discussion

Structural analysis (XRD)

The structural analysis was performed by using an X-ray diffractometer (Rigaku, Tokyo, Japan). The X-ray generator was operated at 40 kV and 100—200 mA. The scanning regions of the diffraction angle (2θ) were 5—80° and Cu Kα radiation were used to collect the spectrum. The step interval was kept at 0.02° with a scan rate of 2.0°/min.

The XRD pattern of CuS nanostructures is shown below which can be indexed to hexagonal CuS structure as compared to the JCPDS database no. 78-0876.

Average particle can be calculated from the XRD pattern using the well-known Debye—Scherrer formula given in the equation (Khan et al., 2013)

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where K is the shape factor, β is full width at half maxima (FWHM) of the highest peak in radian.

$\lambda = 1.540598$ Å, $\beta = 0.4885$ rad, $2\theta = 47.065°$.

Then the calculated particle size is: $D = 17.73$ nm.

SEM analysis

The morphology of the sample was observed by SEM (JEOL JSM-6510LV, Japan). SEM images of the CuS nanostructures are shown in the following figures at different magnification, which clearly reveal that CuS nanoparticles are spherical in shape and uniformly distributed (Priyadharshini and Rajagopal, 2015).

EDS analysis

The elemental analysis was performed by the energy-dispersive X-ray spectroscopy (EDS or EDX) and the spectrum is shown in Fig. 3(a). The EDS spectrum confirms the presence of copper (Cu), sulphur (S), and oxygen (O) in the sample. The bar graph gives the quantitative analysis of the elements in the CuS nanostructures and shown in Fig. 3(b).

Optical characterizations

To characterize the optical properties, UV—visible spectrum analysis is performed by UV—visible dual beam spectrophotometer (Perkin Elmer). Very small amount of the sample is dissolved into the water and solution is sonicated in an ultrasonic bath for 10—15 min to obtain the uniform dispersion. Absorption spectrum is taken in the wavelength range from 150 to 800 nm (Figs. 4 and 5).

The absorption spectrum exhibits a hump at 429 nm which means at this wavelength the material absorbs the UV radiation and its atoms get excited to the upper levels.

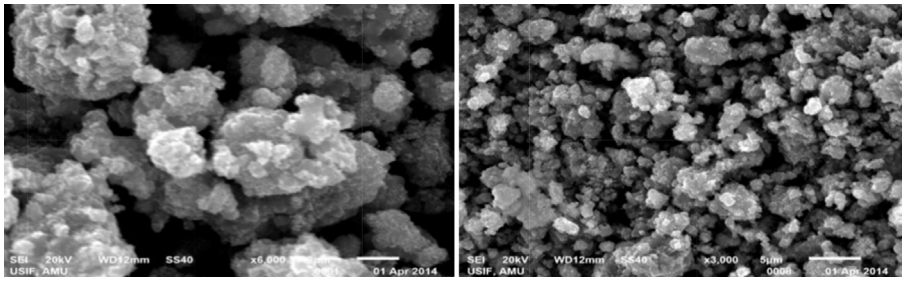

Figure 2 SEM images of CuS nanostructures.

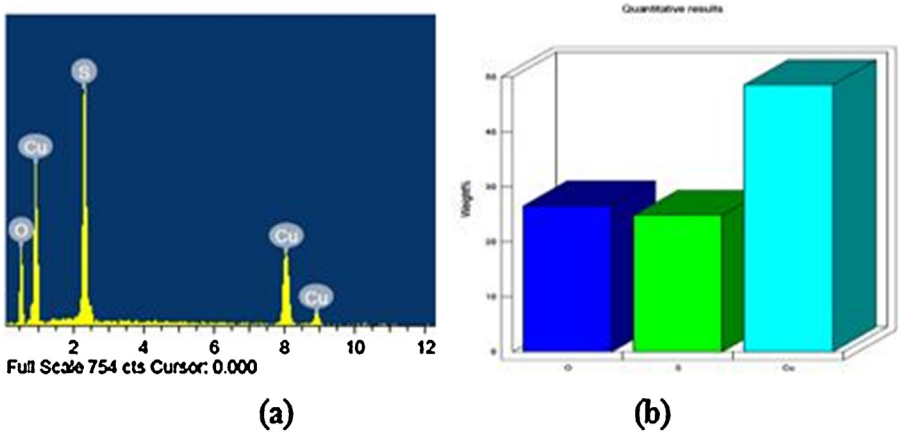

Figure 3 (a) EDS spectrum of the CuS nanostructures and (b) quantitative analysis.

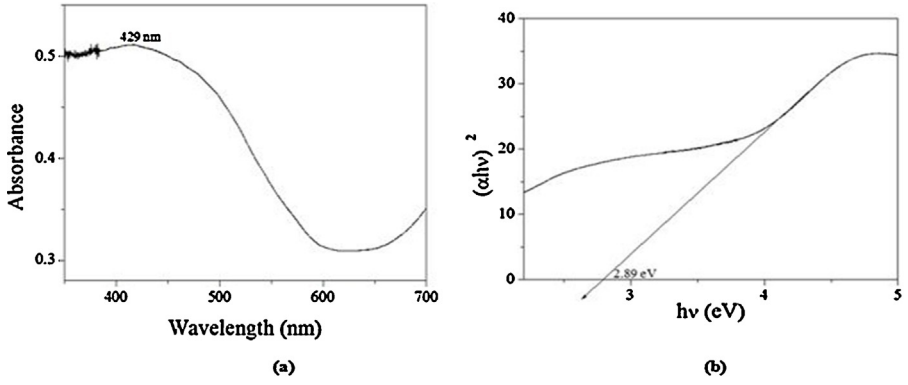

Figure 4 (a) Absorption spectrum of the CuS nanostructures and (b) Tauc plot to determine the band gap.

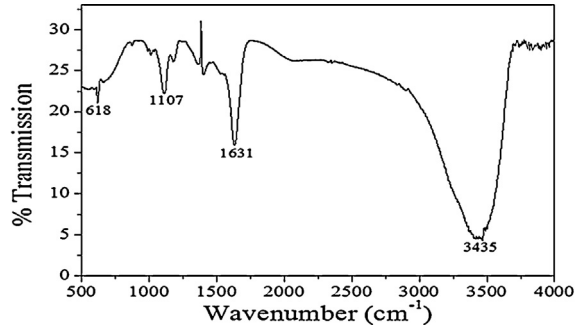

Figure 5 FTIR spectrum of CuS nanostructures.

The energy correspond to this wavelength $E = \frac{hc}{\lambda}$.

Substituting the values, $h = 6.62 \times 10^{-34}$ J s, $c = 3 \times 10^8$ m/s, and $\lambda = 429$ nm.

We get the band gap: $E = 2.89$ eV.

Plotting the Tauc plot (Parveen et al., 2015) and extrapolating the data we found that the band gap is came out to be 2.89 eV.

FTIR analysis

The molecular fingerprinting of the synthesized particles was achieved by FTIR spectrometer (Perkin Elmer). The sample was exposed to the IR radiation in the pallet form. The pallet is made by mixing a very small amount of the sample into potassium bromide (KBr) and the mixture is grinded properly for uniform distribution of the sample into the KBr base. Finally this grinded mixture is pressed in a hydraulic press applying a pressure of ~7 to 8 tons. The spectrum is acquired in the range 4000—400 cm^{-1} and resolution of 2 cm^{-1}. The characteristic band at 3435 cm^{-1} corresponds to the vibration mode of water (OH group) indicating the presence of small amount of water adsorbed on the sample. The band occurring at 1631 cm^{-1} is due to the OH bending of water (Bahadur et al., 2015).

The absorption band located at 1107 cm^{-1} is due to asymmetric stretching of carbonyl (C=O) group. The peaks at 618 signify the existence of Cu—O bond.

Conclusions

In the present work, the CuS nanostructures were synthesized by the sol—gel route. These particles were characterized structurally and optically. The XRD analysis confirms the formation of the structures in the nanometer regime and the discrete peaks are the evidence of the crystalline phase. SEM analyse the morphology of the sample prepared. EDS gives the quantitative elemental analyses and confirms the presence of copper, sulphur and oxygen in the

sample. The UV—visible spectrum of the material shows an absorption peak at 429 nm. Hence the band gap is calculated which comes out to be 2.89 eV.

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