Ultrasound mediated synthesis of CuS nanocrystallites

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We present a unique ultrasonication based method for the preparation of copper sulphide nanoparticles in ambient air using a single precursor complex, which acts as a source of both metal and sulphur. The nanoparticles of 3.31 nm have been prepared successfully by the method and characterized using powder X-ray diffractogram (PXRD), dynamic light scattering (DLS) analysis UV-Vis spectroscopy and fluorescence spectroscopy. The results proved that copper sulphide nanoparticles of hexagonal structure (covellite phase) can be prepared by sonochemical method within a very short reaction time of ~5 min. The band gap of the nanomaterial has also been calculated from absorption spectrum and was found to be 2.36 eV.

Keywords: *copper sulphide nanoparticles; X-ray diffraction; ultrasonication; characterization; band gap*

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1. Introduction

Nanoparticles are generally considered as synthetic atoms as their discrete energy levels are similar to atoms. They are very important class of materials whose optical properties are size dependent when the radius is lower than the exciton Bohr radius. This reveals that the band gap of nanoparticles can be manipulated with the size to adjust desired optical properties, which have drawn attention of researchers working on nanoparticles in the field of nanotechnology. In current years, researchers have given more attention to the preparation of nanoparticles for the applications in a number of fields, such as light emitting diodes and devices [1, 2], room temperature field-effect transistors (FETs) [3], quantum dot/wire lasers [3, 4], biological imaging [5–8], sensors [9, 10], solar cells [11–13], photocatalysts [14, 15]. Another wide range of applications of nanoparticles is due to their size dependent optoelectronic properties [16, 17]. Nanoparticles became an attractive target in photonic and electronic devices because of multiple exciton generation properties [18–20]. The application of multiple exciton generation has the potential to attain maximum efficiency up to

44 % in the 3rd generation photovoltaic cells [12]. Multiple exciton generation means the formation of more than one electron-hole pair by absorption of a photon. When a semiconductor absorbs solar radiation greater than its band gap energy, the photon of the radiation creates an electron-hole pair. The excess energy gets wasted as heat through phonon emission in the bulk of semiconductor but in quantum confined quantum dots, the excess energy produces more electron-hole pairs [12, 21–24]. As far as nanoparticles are concerned, inorganic chalcogenides semiconductor nanomaterials appear as the most important materials for the use in optoelectronic devices. In addition, copper sulphide (Cu_xS), which is a p-type semiconducting material, due to copper vacancies within the lattice, is of particular interest for researchers [25]. It exists in five stable states and these phases are important material for solar cells, solar controllers, nonlinear materials, lithium-ion batteries, gas sensors, and catalysts [26–30]. The green copper sulphide (CuS) – covellite – is more attractive because of additional absorption band in the NIR region [28, 31, 32]. Again, CuS maintains transmittance in the infrared region and shows low reflectance in the visible and high reflectance in the near-infrared region, which makes it an important material for solar energy absorption [33]. Different methods

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of synthesis of copper sulphides reported earlier include synthesis from elements at elevated temperatures [34, 35], microwave-assisted methods [36, 37], thermolysis of molecular precursors [38, 39], hydro/solvothermal synthesis [40–43], microemulsion synthesis [44] and mechanochemical preparation methods [45, 46]. The nanoparticles prepared by the mentioned processes require high temperature and also long duration of the reaction. Ultrasound is now an important tool in the synthesis of nanosized metals, metal oxides and metal chalcogenides. The unique reaction conditions during the process of acoustic cavitation, local increase of temperature up to 5000 K and pressure up to 100 MPa followed by rapid cooling at the rate of 10^9 K/s to bulk temperature [47] enable the formation of nanoparticles with uniform shapes and narrow size distribution. The sonochemical method has been successfully applied for the preparation of a number of metal chalcogenides [48] and the sonochemical synthesis of CuS nanocomposites has also been reported by numerous workers [49–52]. However, in many of the preparation methods they have taken more than one source compound as copper and sulphur precursor. The main aim of our work was the ultrasonication based preparation of copper sulphides using single precursor complex containing both metal ions and sulphur.

2. Experimental

2.1. Materials

Sodium diethyldithiocarbamate, copper (II) chloride, ethanol, dodecylamine, methanol, acetone and chloroform used in this work were purchased from Sigma-Aldrich India. Millipore deionized water obtained from Millipore Milli-Q system was used for washing and preparing aqueous solutions of different chemicals. All chemicals were used as received without further purification.

2.2. Synthesis of precursor complex

First, 1.12 g of sodium diethyldithiocarbamate was dissolved in 50 mL ethanol to prepare sodium diethyldithiocarbamate solution. Then

0.335 g of copper (II) chloride was added to 50 mL ethanol to get copper chloride solution. The sodium diethyldithiocarbamate solution was then added to copper chloride solution dropwise at constant stirring using a magnetic stirrer. The mixture solution was then stirred for 5 min to complete the reaction. The black precipitate formed was then separated by centrifugation and washed 5 times using ethanol. The crystals were purified by recrystallization in chloroform and dried one night at 50 °C in an oven before use.

2.3. Synthesis of CuS nanoparticles

The nanoparticles of copper sulphide were prepared by sonochemical method. The precursor complex (53 mg) was taken into a 20 mL glass reactor and dodecylamine (10 mL) was added to it. Then the suspension was subjected to under ultrasound irradiation at 60 % intensity, using a tip probe based high frequency probe sonicator (20 KHz, Sonic Vibro Cell, USA) for 5 minutes in air atmosphere. During the sonication the temperature recorded was found to be 150 °C. The suspension was then kept at room temperature for 5 minutes. Then 5 mL chloroform and 5 mL methanol were added into the suspension and the whole content was centrifuged at 4000 rpm. The supernatant containing copper sulphide nanoparticles was then mixed with an equal volume of methanol and again centrifuged at 7000 rpm to isolate the particles. The nanoparticles were purified using methanol and chloroform. The purified material was then divided into two parts, one part was placed on a glass slide (2 cm × 2 cm) for PXRD studies and the other part was dispersed in chloroform for absorbance, photoluminescence and DLS studies.

2.4. Characterization

The powder X-ray diffraction measurements (PXRD) were performed on a Siemens (Cheshire, UK) D5000 X-ray diffractometer equipped with $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA with a standard monochromator equipped with a Ni filter, in the range of 10° to 70° , using the step size 0.013° and time step 13.6 s. Dynamic light scattering (DLS)

characterization was done with a Malvern Zetasizer Nano Series (Nano ZS). UV/Vis-DRS data were recorded on UV/Vis-DRS spectrophotometer Carry-5000. Time-resolved fluorescence measurements were carried out using HORIBA Jobin Yvon spectrofluorometer.

3. Results and discussion

The powder X-ray diffractogram of the prepared sample was obtained using Siemens Cheshire, UK D5000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation to find the crystalline phase of the synthesized particles. The pattern shown in Fig. 1 contains peaks assignable to (1 0 2), (1 0 3), (1 1 0), (1 0 4) and (1 1 6) planes of CuS hexagonal structure, covellite phase corresponding to 2θ at 29.4, 32.80, 48.0, 52.8 and 59.3°, respectively. Similar results have also been reported by Kristl *et al.* [53] but they have taken two precursor compounds for copper and sulphur.

Fig. 1. XRD pattern of CuS quantum dots.

All the diffraction peaks can be indexed to the hexagonal phase of CuS (JCPDS No. 06-0464). The crystallite size of the nanoparticles was calculated by Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where, k is the shape factor, λ is the X ray wavelength, β is the full width at half maximum of corresponding peak (FWHM), θ is the Bragg angle and D is the mean size of the particle. The calculated size was 3.31 nm. The hydrodynamic diameter was measured by DLS (Zetasizer Nano-ZS, Malvern instrument, UK) for the CuS nanoparticles and was found to be 15 nm (Fig. 2). The result revealed that the smaller sized CuS crystallites than

estimated from the XRD were slightly aggregated in the suspension.

Fig. 2. The size distribution of the CuS quantum dots dispersed in chloroform.

The UV-Vis adsorption spectrum of the prepared sample was recorded using UV-Vis-DRS (Varian Cary-5000) spectrophotometer. The absorption spectrum (Fig. 3) shows a broad absorption peak in near IR region at 960 nm and a shoulder near 400 nm. The absorbance never reaches zero, which is characteristic of formation of covellite CuS nanoparticles [54, 55]. Also the longer absorption end is endorsed by the scattering effect, free-carrier intra-band absorbance [56], generation of midgap states and transitions to the conduction band [25]. The optical band gap energy (E_g) of CuS nanoparticles was also measured from absorption spectra and it was found to be 2.36 eV (525 nm) which is greater than the optical band gap energy (E_g) of bulk CuS (2.0 eV). The widening of the band gap (0.36 eV) as compared to bulk may be attributed to quantum size effect [57].

The fluorescence spectrum of the CuS nanoparticles was taken with a Xe lamp at 350 nm excitation at room temperature. The spectrum (Fig. 4) shows a peak at 420 nm which is considerably blue shifted relative to the bulk samples, indicating a quantum size effect. This feature reveals that the nanoparticles exhibit quantum-confined effects and size-tunable optical properties [58].

4. Conclusions

A facile synthesis of copper sulphide nanoparticles containing non-toxic element was investigated by sonochemical method taking diethyldithiocarbamate complex of metal ion as precursor.

Fig. 3. Absorbance spectrum of CuS quantum dots.

Fig. 4. Photoluminescence spectrum of CuS quantum dots.

The prepared sample was characterized by DLS, XRD, UV-Vis and fluorescence spectroscopy to confirm the formation of nanoparticles. The results proved that the formed CuS nanoparticles were slightly aggregated in chloroform. This synthetic approach is simple, requires short reaction time for the formation of nanoparticles and eliminates the requirement of heating at high temperature for decomposition of the complex. Hence, it could be useful in synthesizing other compositions as well.

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