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Colloidal synthesis of copper cadmium sulphide ($CuCdS_2$) nanoparticles and its structural, optical and morphological properties

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ABSTRACT

Oleylamine mediated $CuCdS_2$ nanoparticles were synthesized by the colloidal hot injection method at 230 °C. Structural analysis reveals that the nanoparticles exhibit wurtzite phase with high crystallinity. The average crystallite size of the nanoparticles was calculated as 40 nm. Optical band gap of the synthesized nanoparticles was calculated from UV-vis absorption spectrum as ~1.70 eV. Nanorods and nanoplates like morphologies with well-defined boundaries of $CuCdS_2$ nanoparticles were observed from scanning electron microscope analysis. Purity of the synthesized nanoparticles was confirmed using energy dispersive X-ray analysis. Vibrational modes of $CuCdS_2$ nanoparticles were observed from the Raman spectroscopy analysis. X-ray photon spectroscopy analysis confirms the oxidation states of the elements present in the nanoparticles. The possible mechanism involved in the formation and morphology of $CuCdS_2$ nanoparticles was discussed.

1. Introduction

Synthesis of shape and size modified semiconductor nanoparticles has attracted many researchers in recent years. Due to its significant size dependent physical properties that can be used for various applications, such as photovoltaic, light emitting diodes (LED) and nanoelectronics [1]. Especially, the electrical conductivity will be higher in elongated nanostructures than in spherical nanoparticles. Thus, electrical conductivity of the semiconductor nanoparticles strongly depends on its shape and size [2]. For modifying shape and size of the nanomaterials with controllable atmosphere, colloidal method gives considerable results by varying concentration of precursors, complexing agents, pH and temperature [3]. There are many less toxic; non-phosphine solvents that were utilized for the synthesis of nanoparticles. In recent years, oleylamine (OLA) is preferred by many researchers due to its versatile usage, such as solvent, surfactant, and as an electron donor in high temperatures. More often, OLA may act as a mild reducing agent at higher temperature [4]. In particular, the affinity of OLA to the metal cations through amidogen (NH_2) gives significant changes in the morphology of resulting nanoparticles [3].

Cadmium sulphide (CdS) is a n-type semiconductor material used as a window layer material in heterojunction solar cells due to its wide band gap (2.42 eV) [5]. Also, it has a wide range of applications in laser materials, photo resistance, light emitting diode, nonlinear optical devices, etc., [6,7]. Copper sulphide ($Cu_{2-x}S$ ($0 \le x \le 2$)) is another interesting semiconducting material with different phases, i.e chalcocite (Cu_2S), dijurleite ($Cu_{1.94}S$), digenite ($Cu_{1.8}S$), covellite (CuS), etc., [8]. It has the wide range of applications which strongly depends on final phase formed after synthesis [9,10]. In addition to that, $Cu_{2-x}S$ nanoparticles have an interesting property of exhibiting localized surface plasma resonance (LSPR) associated with absorption in near-infrared region (NIR) which are normally observed in noble metals [11]. This raises the interest of researchers into knowing the carrier dynamics of $Cu_{2-x}S$ nanoparticles. In addition, physical properties of $Cu_{2-x}S$ nanoparticles vary with changes in their shape and size [12]. Various shapes of CdS (nanorods) and $Cu_{2-x}S$ (nanorods, nanoplates, nanoflakes, flowerlike, etc.) have been synthesized via OLA assisted colloidal hot injection method [3,13]. It ensures the possible route to synthesize copper and cadmium based chalcogenides using OLA.

Conjoining CdS and CuS provide unique physical and chemical properties to elevate the applications such as solar cells and optoelectronic devices. For example, CdS:Cu/ CdS homostructured solar cell by vacuum process showed an efficiency of 8.5% [14]. Further developments in the CdS/CuS heterostructure were hindered by the diffusion of cadmium and copper. Ternary and quaternary copper chalcogenides have more stability and efficiency when compared with binary [15,16]. In addition, it was reported that copper impurities behave as an acceptor in CdS and changes its resistivity and band gap. Tuning the

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concentration of copper incorporation in CdS sites, changes n-type semiconducting property to p-type [17]. Tsamouras et.al, reported that synthesis of ternary $CuCdS_2$ without structural confirmation and its use in heterojunction photovoltaic device [18]. Khan et.al, observed that CuCdS nanocrystals with zinc blende structure can be used in LED applications since the synthesized nanoparticles possessed high solid state luminescence [19]. The optical energy band gap of CuCdS thin films prepared via chemical bath deposition method lies in the range of 2.45 eV to 2.2 eV [20]. Various synthesis methods have been employed to synthesize copper and cadmium based chalcogenides such as colloidal, solvothermal methods, one-pot heating up method, etc. [21]. However, synthesis of ternary 2D nanostructures such as, nanoplates or nanorods with uniform size and well defined shape remains a challenge [22,23]. In order to overcome the challenge, colloidal hot injection method has gained much attention for synthesizing of semiconducting chalcogenides since the resultant particles have interesting physical properties for applications such as solution processable photovoltaic, photocatalysis, photothermal therapy, etc., [15,24]. In this work, copper cadmium sulphide ($CuCdS_2$) nanoparticles were synthesized by colloidal hot injection method under controlled atmosphere using OLA as a solvent. Structural and optical properties of synthesized $CuCdS_2$ nanoparticles were analyzed and the mechanism over the formation of nanoparticles was discussed.

2. Experimental details

2.1. Materials

Synthesis of $CuCdS_2$ nanoparticles was carried out using copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$), cadmium chloride ($CdCl_2$), elemental sulfur as precursors and oleylamine (OLA) as complexing agent. All the chemicals were in analytical grade and used without further purification.

2.2. Synthesis of $CuCdS_2$ nanoparticles

A three-necked flask with 20 ml of OLA, attached with condenser was vacuumed for one hour and then nitrogen gas was purged into the flask. After that, 1 mM of $CuCl_2$ and 1 mM of $CdCl_2$ are added in with OLA and heated up to 180 °C under nitrogen atmosphere. During this stage, a yellow coloured Cu- Cd oleate complex was formed in the flask. In the mean time, 2 mM of elemental sulfur was refluxed with about 20 ml of OLA at 150 °C and injected into the Cu-Cd-oleate complex. The entire mixture was heated further up to 230 °C. After the addition of sulfur precursor into the oleate complex, change in colour was observed from yellow to black, which indicates the formation $CuCdS_2$ nanoparticles. The obtained product was kept at 230 °C for 5 h and brought to room temperature. The particles were precipitated by addition of isopropanol from the colloidal medium and centrifuged. The product was further washed with ethanol and acetone several times for removing byproducts. Then, the product was dried in vacuum for further analysis. The various stages involved in the reaction are given by the following Eqs. 1 and 2.

$$CuCl_2.2H_2O + CdCl_2 + \text{Oleylamine} \xrightarrow[180℃]{} Cu - Cd - \text{Oleate} \quad (1)$$

$$Cu - Cd - \text{Oleate} + 2S \xrightarrow[230℃]{} \quad (2)$$

And the overall reaction is given by the Eq. (3).

$$CuCl_2.2H_2O + CdCl_2 + 2S \xrightarrow[\Delta 230℃]{} CuCdS_2 + \text{by products} \quad (3)$$

The experimental steps involved in the synthesis of $CuCdS_2$ nanoparticles are given in Fig. 1.

2.3. Characterization details

Structural property of the synthesized $CuCdS_2$ nanoparticles was characterized using Bruker d2 phaser X-ray diffractometer with Cu kα radiation at an operating voltage of 30 kV with 10 mA current. UV-visible spectroscopy analysis of synthesized nanoparticles was carried out using JASCO V-650 spectrometer (DRS). Morphology of the nanoparticles was imaged using FEI quanta FEG 200 high resolution scanning electron microscope and FEI, TECHNAI G2, 30 S-twin D905 high resolution transmission electron microscope. Oxidation states of the elements present in the nanoparticles were analyzed using AMICUS ESCA 3400 X-ray photoelectron spectrometer.

3. Results and discussion

3.1. Structural analysis

The X-ray diffraction pattern (XRD) of synthesized $CuCdS_2$ nanoparticles is given in Fig. 3. The presence of high intensity narrow diffraction peaks indicates that synthesized nanoparticles have good crystallinity. It was observed from XRD that the $CuCdS_2$ nanoparticles consist of both $CuCdS_2$ phase and CuS phase. The $CuCdS_2$ phase exhibits higher intensities in the XRD pattern compared to the lower intensities of the CuS phase. CuS binary peaks were indexed with JCPDS No. 30-0505. The high intensity peaks were compared with wurtzite CdS phase (JCPDS card No. 80-0006). It was observed that the diffraction peaks were corresponding to $CuCdS_2$ shifted to higher angles compared with CdS nanoparticles. The shift indicates that shrinkage due to copper substitution in CdS site that results in shifting of peaks to higher angle [19]. It is well known that copper has a smaller atomic radius (1.35 Å) than cadmium (1.51 Å) [17]. High intensity reflections were observed at 2θ (degrees) values of 24.92, 26.61, 29.89, 36.72, 43.81, 47.94, 51.95 which were indexed using PowderX software to the respective planes of (100), (002), (101), (102), (110), (103), (112). The presence of (100), (002) and (102) planes corresponds to wurtzite phase with a hexagonal structure [25]. The prominent peak was located at (002) plane, which indicates that the plane extended in c-axis [26]. Lattice strain and crystallite size of the nanoparticles were calculated from the diffraction data using Williamson-Hall plot (W-H). W-H plot was drawn between sinθ and βcosθ in x and y-axis respectively (Fig. 4) using the Eq. (4) [27].

$$\beta\cos\theta = \frac{k\lambda}{D} + 4\varepsilon\sin\theta \quad (4)$$

Where, β is full width at half-maximum, λ is the wavelength of the X-ray, D is the average crystallite size and ε is the lattice strain of the material. From the W-H plot, slope of the linear fit is strain experienced by the synthesized nanoparticles and intercept determines the average crystallite size of $CuCdS_2$ nanoparticles. In this present work, the calculated lattice strain was 0.003 and calculated average crystallite size was 40 nm. Positive value of strain indicates the tensile nature of synthesized $CuCdS_2$ nanoparticles. The dislocation density of the nanoparticles was determined using Williamson and Smallman's formula which is given in Eq. (5) [27].

$$\delta = \frac{1}{D^2} \quad (5)$$

Where, δ is dislocation density and D is average crystallite size of the nanoparticles.

The calculated dislocation density is 1.33×10^{14} lines/m.

The lattice values were calculated for the nanoparticles using Eqs. (6) and (7) [28].

$$a = \frac{\lambda}{\sqrt{3}\sin\theta}\sqrt{h^2+hk+k^2} \quad (6)$$