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Original Research Article

Amino acid (L-alanine) capped CuS nanoparticles: Synthesis and characterization

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ABSTRACT
We report synthesis and characterization of CuS nanoparticles (NPs) capped using l-alanine amino acid by simple co-precipitation method. The samples in powder form were characterized by X-ray diffractometry (XRD), Energy dispersive X-ray spectroscopy (EDS), High-resolution transmission electron microscopy (HR-TEM), ultra-violet visible (UV-vis) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. Formation of desired phase was confirmed by XRD data and purity of the sample was confirmed by EDS spectrum. HR-TEM micrographs confirms the formation of NPs with good morphology. The diffraction peaks in the XRD spectra are found to be broadened indicating narrow crystallite size which was found to be 15 nm. UV-vis spectra show two absorption peaks due to excitonic absorption and LSPR. Blue shift in the maximum absorption peaks is evident and the shift is more prominent for the CuS sample prepared using highest concentration of l-alanine justifying its role in the efficient capping agent. FT-IR spectrum confirms the presence of amino-acid group.

1. Introduction

Research in nanoscience and nanotechnology is gaining its interests day by day due its infinite applications in various fields e.g. optoelectronics, sensors, imaging devices, lasers, communications, etc. The complete technology in the nano regime is based on fact that particles with at least on dimension in nano-range show extra-ordinary properties due quantum confinement effect and high surface to volume ratio [1-6]. Several authors have shown that metal and metal oxide nanoparticles possess outstanding properties [7, 8]. Non-oxide nanoparticles such as metal sulfides took special attention due to their advanced NLO properties. Metal sulfide nanoparticles (NPs) that include silver sulfide, CdS, ZnS and CuS are also found to show interesting properties in various fields [9-11]. Several surface modifying agents (capping agents) are used to control the particle size and limit the agglomeration. Amino acids have been used as capping agent by many authors due to their easy availability, low cost, biodegradability, non-toxicity and environment friendly properties [12]. We report synthesis of CuS NPs using L-alanine as capping agent by simple co-precipitation method in this paper.

2. Materials and methods

2.1 Materials

CuS NPs have been synthesized using low-cost simple chemical co-precipitation method. All chemicals used were of analytical reagent grade and used without further purification. Copper chloride dihydrate ($CuCl_2.2H_2O$), sodium sulfide flakes (Na_2S) and ethanol, all AR grade, were procured from SD-fine Chemicals, Mumbai. L-alanine was purchased from Sigma Aldrich, USA.

2.2 Methods

Stock solutions of 1M $CuCl_2.2H_2O$, 1M Na_2S and 1M L-alanine in double distilled water (DDW) have been prepared in separate beakers. For the synthesis of CuS NPs without using capping agent (sample name CS-Pure), 10 ml $CuCl_2.2H_2O$ from stock solution is added into the beaker containing 150 ml DDW at 70°C. The solution is kept under vigorous constant stirring using magnetic stirrer and temperature is maintained. The temperature is brought down to 20°C and then, 10 ml Na_2S from stock solution is added into the resultant solution dropwise under vigorous stirring. Black color precipitate (ppt) is obtained as soon as we add Na_2S confirming the formation of CuS NPs. The resultant solution is stirred for another 30 mins.

For the synthesis of CuS NPs using L-alanine as a capping agent (sample name CS1), 10 ml $CuCl_2.2H_2O$ from stock solution is added into the beaker containing 150 ml DDW under constant stirring at 70°C. Then, 3 ml L-alanine was added into the solution dropwise and solution is stirred for 30 mins. The temperature is brought down to 20°C and then, 10 ml Na_2S from stock solution is added into the resultant solution dropwise under vigorous stirring to get black ppt of CuS NPs. The resultant solution is stirred for another 30 mins. Two more

samples (CS2 and CS3) have been prepared adding 6 ml and 10 ml L-alanine into the solution before addition of Na_2S.

The solution containing CuS NPs is centrifuged at 4000 rpm using REMI centrifuge machine model 4R-C and washed with DDW several times. The obtained ppt was then dried in hot air oven at 80°C for 4h. The dried powder then crushed into fine powder using agate mortar pestle. As synthesized samples of CuS NPs are shown in Table 1.

Table 1: CuS NPs synthesized using L-alanine as a capping agent

Sample	$CuCl_2$ (1 M)	Na_2S (1 M)	L-alanine (1 M)
CS-Pure	10 ml	10 ml	--
CS1	10 ml	10 ml	3 ml
CS2	10 ml	10 ml	6 ml
CS3	10 ml	10 ml	10 ml

2.3 Characterizations

Prepared CuS NPs were subjected to structural characterization by X-ray diffraction (XRD) using Rigaku diffractometer Miniflex II with nickel filtered CuK_α radiation (λ = 1.54059 Å). Energy dispersive X-ray spectroscopy (EDS) was performed by Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) Model JSM-7600F, Japan. Ultraviolet visible (UV-vis) spectroscopy was performed using UV-visible spectrophotometer (BLK-C-SR, Stellarnet, USA). Fourier transform infra-red (FT-IR) spectra were recorded using IR double beam spectrophotometer, Shimadzu, Japan. High resolution transmission electron microscopy (HR-TEM) has been performed using FEG-TEM 300 KV Model FEI Tecnai G2, F30.

3. Results and discussion

3.1 Structural study using XRD, EDS and HR-TEM

Figure 1 shows XRD spectrum of as synthesized powder samples of CS-Pure and CS3 in the range of 10° - 90°. The spectrum clearly indicates the formation nanoparticles as the diffraction peaks show broadening [13]. The peak broadening is more in sample CS3 which is synthesized using L-alanine as capping agent than that of the sample CS-Pure synthesized without capping agent. This also proves the role of L-alanine as capping agent. All the peaks are perfectly matched with CuS phase with PCPDF card no. 9000523. No peaks corresponding to impurities were seen validating the purity of our prepared samples. Debye-Scherrer formula was used to calculate particle size of prepared NPs. The average particle size was found to be 15 nm for sample CS3 and 22 nm for sample CS-Pure. Figure 2 depicts the EDS spectrum of CuS NPs for the sample CS3 indicating the peaks corresponding to Cu and S only confirming the purity of the prepared sample. HR-TEM micrographs of CuS NPs are shown in Figure 3 confirming the nanostructure formation having uniform spherical morphology. The particle size calculated using XRD also agrees with particle size seen from HR-TEM images.

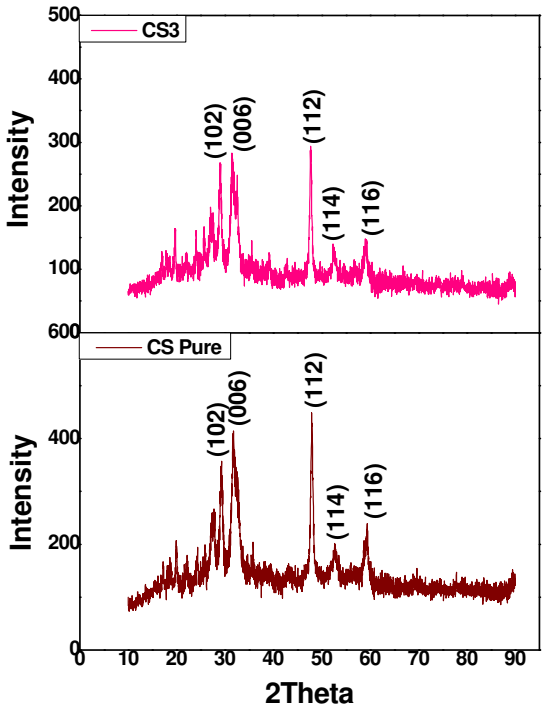

Figure 1: XRD spectra of CuS NPs.

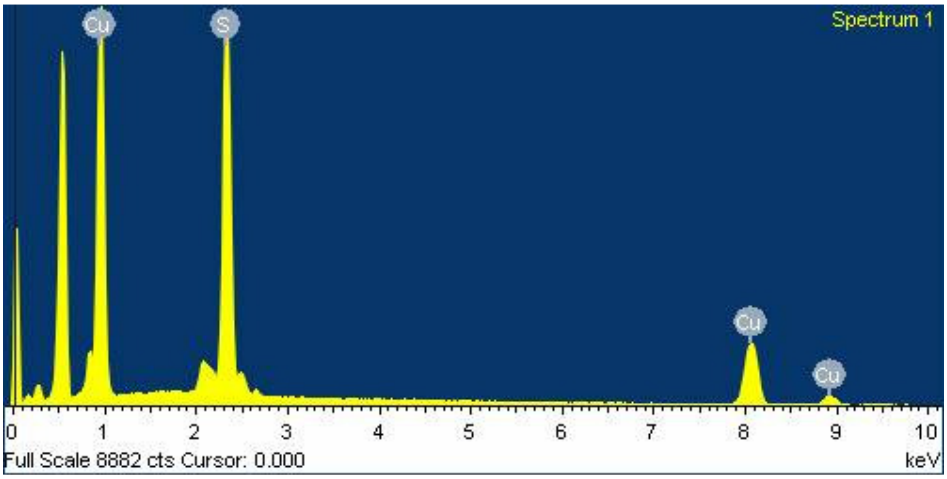

Figure 2: EDS spectrum of CuS NPs.

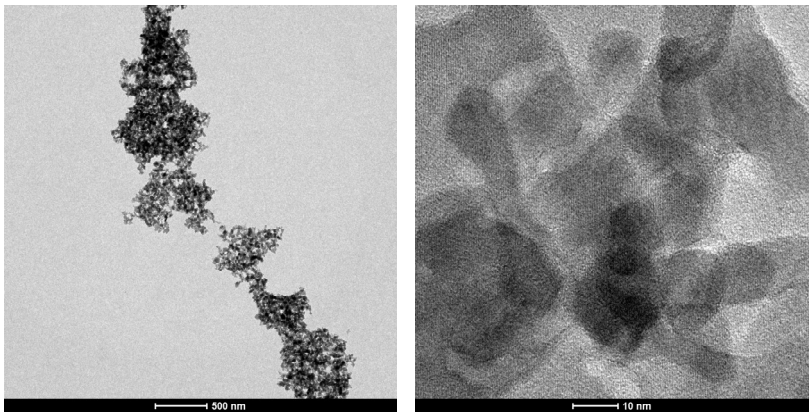

Figure 3: HR-TEM micrographs of CuS NPs.

3.2 UV-vis spectroscopy

Figure 4 depicts the absorption spectrum of synthesized CuS NPs in UV-vis-NIR region. Two absorption peaks can be identified. One peak around 522-530 nm is seen in the UV-vis region which can be attributed to the excitonic absorption in the CuS NPs [14, 15]. It can also be seen that, the absorption peak is shifting towards blue end as the concentration of l-alanine is increased which prove the effective role of l- alanine as capping agent since decrease in particle size is observed with increase in the concentration of l- alanine. The second absorption edge is observed around 745-750 nm which can be attributed to the absorption due to local surface plasmon resonance (LSPR) in the nano-phase of CuS [16-20].

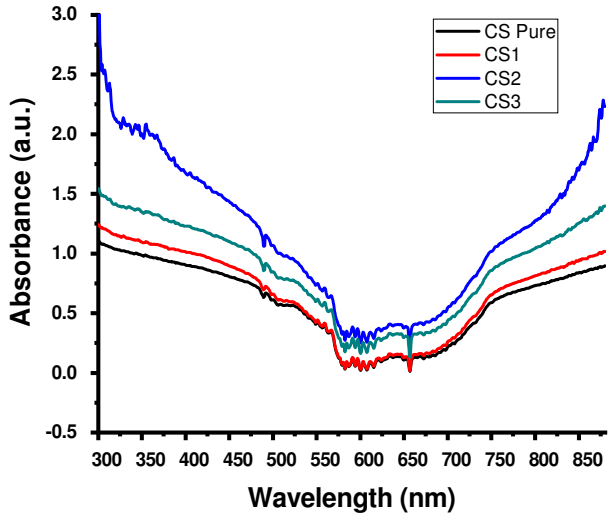

Figure 4: UV-Vis absorption spectra of CuS NPs.

Table 2: Absorption wavelengths for CuS NPs

Sample	Excitonic absorption wavelength (nm)	LSPR absorption wavelength (nm)
CS-Pure	530	750
CS1	528	747
CS2	525	745
CS3	522	745

3.3 FT-IR spectroscopy

The FT-IR spectrum of l-alanine capped CuS NPs (Sample CS3) was recorded and shown in Figure 5. The peaks appearing at 626 cm^{-1} belong to Cu-S vibrations [21, 22]. Symmetric and asymmetric stretching of O-H, N-H, and C-H bonding may have caused the broad absorption band from 2294 to 3737 cm^{-1}. Peak at 1682 cm^{-1} is due to C=O stretching. Vibrations of COO-group may generate peaks at 1540 cm^{-1}. Peak at 1133 cm^{-1} is due to C-O bonding. COO- bonding again gives peak at 626 cm^{-1} and torsional modes of CNH_2 generates peak around 499 cm^{-1}. All these peaks confirmed the presence of l-alanine and CuS.

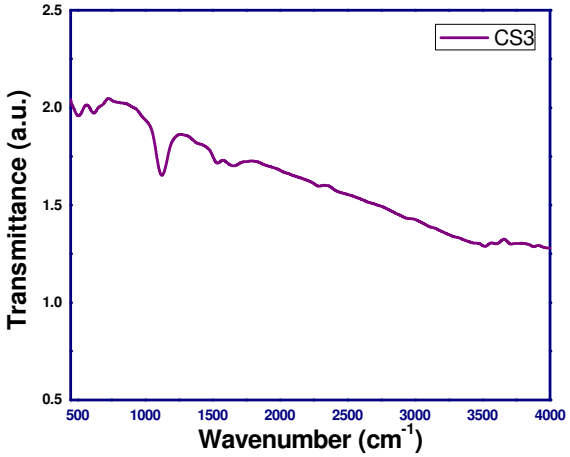

Figure 5: FT-IR spectrum of CuS NPs.

4. Conclusions

CuS NPs capped with l-alanine were successfully synthesized using low-cost simple co-precipitation method. Structural studies were performed using XRD, EDS and HR-TEM and confirmed the formation of CuS Covellite phase with no evidence of any impurity. Average particle size was found to be around 22nm for CuS NPs (without capping agent) and 15nm for CuS NPs capped using l-alanine. Linear optical studies using UV-vis spectroscopy confirmed the occurrence of two absorption peaks due to excitonic absorption and LSPR. FTIR spectra confirmed the presence of functional groups associated with CuS.

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