Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 2, Issue 19; October-December, 2015, pp. 1684-1687

http://www.krishisanskriti.org/Publication.html

Excess Sulphur Induced Structural and Optical Properties of Green Synthesized CuS Nanostructures

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Abstract—*In the present work, the Cu/S ratio was maintained by mixing the respective ion complex (0.005M) in volumetric ratio during the synthesis. Both starch and glucose capped CuS show a superior structural and optical properties, when the ratio is kept at 1:2 and 2:3 respectively. The XRD exhibits the formation of polycrystalline CuS with hexagonal structure. The HRTEM shows a spectacular spindle type particle distribution for CuS/starch whereas a well defined distribution of nanorods for CuS/glucose. The UV-vis absorption studies show good blue shift of absorption edge for all synthesized materials with an enhancement of band gap to 3 - 3.4eV as visible from the Tao-plot. The photoluminescence (PL) shows a near UV emission around 367 nm to 396nm. The glucose capped CuS exhibits a spectacular enhancement of PL intensity compared to that of CuS/starch.The Cu/S volumetric ratio is also confirmed from the compositional analysis of EDAX.*

1. INTRODUCTION

Polycrystalline metal sulphide is considered as an advanced functional material that shows novel optical & electrical properties. Owing to quantum size effects & surface effects, nanostructure materials can display novel optical, electrical, chemical and structural properties that might find important technological applications [1-4]. Nanostructure transition metal sulphides such as Cds, ZnS, HgS & PbS exhibit very unusual physical & chemical properties compared to those of their bulks [5]. Copper sulphide is a good prospective opto-electronic p-type material. It is potentially used in solar cells, IR-detectors, optical filters & other low cost devices owing to its high absorption coefficient ($10^4 cm^{-1}$) & narrow band gap (1.2eV). Copper sulphide has very complex crystal chemistry owing to its ability to form various sub-stoichiometric compounds ranging from Cu_2S at the copper rich side to CuS_2 at the copper deficient side such as CuS, $Cu_{1.96}S$, $Cu_{1.96-}S$, $Cu_{1.8}S$, Cu_7S_4 & Cu_2S[6,7]. The amorphous brown chalcocite (Cu_2S) & the green-black crystalline covellite (CuS) phase are of special interest owing to its metal-like electrical conductivity [8]. Nanoscopic copper sulphide exhibits interesting structural & optical characteristics depending upon different growth parameters such as molar concentration, temperature, capping agents, surfactants, precursor solution composition etc.

Sulphur ions may play a key role in determination of various copper sulphide nanostructures particularly when sulphur is used in excess. Keeping above aspects, an experimental work on the synthesis & characterization of copper sulphide nanostructures has been undertaken and the role of sulphur in correlation with the optical properties has been highlighted in this paper.

2. EXPERIMENTAL

2.1 Synthesis

Two green capping materials starch and glucose were used to synthesize the CuS at room temperature (~30°C), keeping molar concentration at 0.005M by a simple chemical route. First of all, 3% starch was dissolved in 100ml deionised water in a container using magnetic stirrer. Equimolar (0.005M) copper acetate monohydrate ($(CH_2COO)_2Cu.H_2O$) and thiourea (H_2NCSNH_2) were dissolved in 3% starch mixed deionsed water in the volumetric ratio 1:2 in two separate containers under continuous stirring by a magnetic stirrer. Ammonia (aq.) was added to the starch mixed copper ion complex where thiourea solution was added dropwise for the formation of final copper sulphide matrix solution. The synthesized copper sulphide solution became greenish in color with black precipitate. Similar procedures were adopted to synthesize starch capped copper sulphide in the ratio 2:1 and glucose capped copper sulphide in the ratio 2:3 & 3:2 respectively.

Glass substrates were used to deposit thin film of copper sulphide. The glass substrates were cleaned over which the thin films of copper sulphide were casted. The films were taken for characterizing with XRD (X-ray diffraction) and the filtrate solution for other optical measurements.

2.2 Characterization

XRD and high resolution electron microscopy (HRTEM) techniques were used to determine the structural characterization of the synthesized nanoparticles. The X-ray diffractograms were recorded using copper Kα radiation (λ=1.5406Å). The X-ray tube was operated at 40kV 40mA. The 2θ was varied from 0^o to 80^o with scanning rate 0.05^o. The TEM morphology was recorded using JEM 2100 (Jeol Electronic Microscope) at accelerating voltage 200 kV and beam current 102 μA. USB-2000 UV-visible spectrometer was used to measure the optical spectra of nanoparticles over the range 300nm to 700 nm. The photoluminescence (PL) spectra were recorded in the wavelength range 350 nm to 700 nm. The Cu/S volumetric ratio was also confirmed from the compositional analysis of EDAX.

3. RESULTS AND DISCUSSION

3.1. Structural characterizations

Fig.1. shows the XRD pattern of the glucose capped deposited copper sulphide thin film of the Cu/S volumetric ratio 3:2 in an alkaline medium (pH~10). The XRD pattern of the deposited copper sulphide exhibits weak diffraction peaks superimposed on glucose matrix. The diffraction peaks at 14.8^o & 21.4^o corresponding to (101) & (200) atomic planes were due to glucose matrix. This type of weak diffraction peaks were also reported by other workers particularly when the sample is embedded in a polymer matrix like PVA & PNIPAM (poly N-isopropy lacrylamide [9, 10, 11]. The XRD showed prominent (102), (103) &

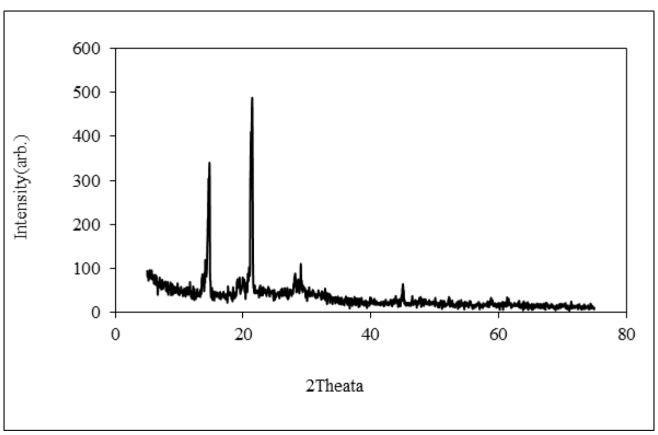

Fig. 1: XRD pattern of glucose capped CuS thin film at Cu/S ratio 3:2

(110) planes of CuS covellite phase corresponding to 2θ at 44.7^o, 59^o & 49.8^o. The other prime peaks at 28^o & 29^o were corresponding to (400) & (412) planes of chalcocite (Cu_2S). This was confirmed from standard JCPDS data no. 2-1272 for covellite (hexagonal) & chalcocite copper sulphide respectively [12, 13].

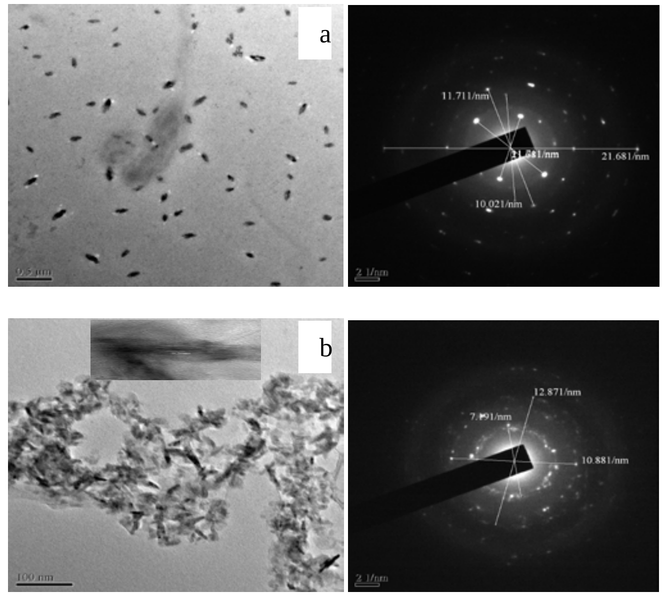

Fig. 2: HRTEM images of a. Spindle type nanoparticle, b. Nanorods with corresponding SAED pattern of Cu/S ratio 1:2 & 2:3 of the starch & glucose capped matrix respectively. d-value (inset).

The HRTEM morphology clearly shows the fine CuS nanoparticles embedded in both starch & glucose matrix while the selected area electron diffraction (SAED) pattern shows a central halo with concentric broad rings, the broadness, possibly originating from the confinement of nanocrystallites embedded in the starch & glucose matrix. A close view of the HRTEM morphology shows a spectacular spindle type particle distribution for CuS/ starch of Cu:S=1:2 (Fig.2a) whereas a well defined distribution of nanorods for CuS/glucose of Cu:S=2:3 (Fig.2b). The spindle particles have average dimensions of 200nm that are actually the agglomerates of nanoparticles having diameter 13nm. The average size of the nanorods is estimated to be 17 to 40nm in length & 7 to 10 nm in thickness. It is observed that the capping agents play an important role in the confnement of nanorods. The SAED of nanorods shows different orientations. It shows (110) atomic plane corresponding to hexagonal structure. The rings are prominent which indicates a good crystallinity possessed by the synthesized nanoparticles. The HRTEM also shows the d-value of 0.26nm in nanorods(Inset). This indicates that the growth direction is along that atomic plane corresponding to that d-value.

3.2. Optical characterization

The optical properties of CuS nanostructures were studied by UV-visible absorption spectroscopy and photoluminescence spectroscopy to further assess their quality. The UV-vis absorption studies show good blue shift of absorption edge for all synthesized materials. The band gap is enhanced to 3-3.4 eV. Fig.3 shows the typical absorption spectra of CuS/starch deposited nanostructure of Cu/S ratio 1:2 and the corresponding $(\alpha h\nu)^2$ versus hν plot (Tao plot) is linear which indicates that the mode of transition is of direct nature [I4]. Extrapolation of these curves to zero absorption coefficient value (α=0) gives the optical band gap energy. The UV-vis absorption spectra show a wide absorption upto 700nm. In constrast to the absorption spectra, the photoluminescence spectra of the copper sulphide show a near UV emission around 367nm to 396nm. Fig.4 shows sharp emission peak at about 369nm (3.34 eV) of the typical Cu/glucose nanorods synthesized at Cu/S volumetric ratio 2:3 corresponding to exciton emission peak. The emission

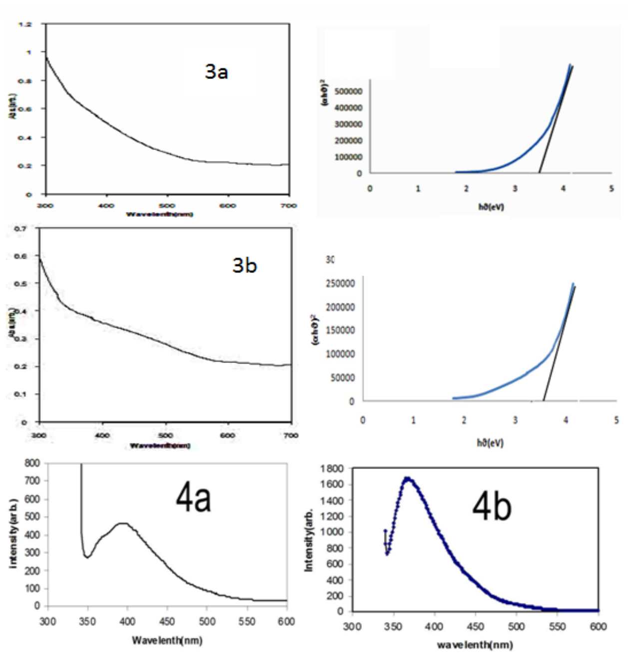

Fig. 3: UV-vis. and corresponding $(\alpha h\upsilon)^2$ – hυ plot of a. CuS/starch (Cu:S= 1:2) & b. CuS/glucose (Cu:S= 3:2). Fig.4 Corresponding PL spectra of CuS/Starch & CuS/glucose (Cu:S = 1:2, 2:3)

bands showed in the spectra can be attributed to band gap emission and the strong band gap emission demonstrates the high crystalline nature of the as-synthesized nanorods [15]. The glucose capped CuS exhibits a spectacular enhancement of PL intensity compared to those of CuS/starch. The intensity of photoluminescence peak is also high which is attributed to the good aspect ratio of nanorods. Further, as the surface to volume ratio is high, it induces large surface state. This surface state contributes to the enhancement of photoluminescence intensity. Further, the PL peak is also symmetric one which reveals a uniform distribution of well defined nanorods [16].

3.3.Elemental composition from EDAX microanalysis

The sample was taken in a beaker with acetone and sonicated for 15 minutes. 15 micro liter of (sample + acetone) mixture was dropped on an aluminium foil coated glass substrate and dried in an electronic oven for 60 minutes at

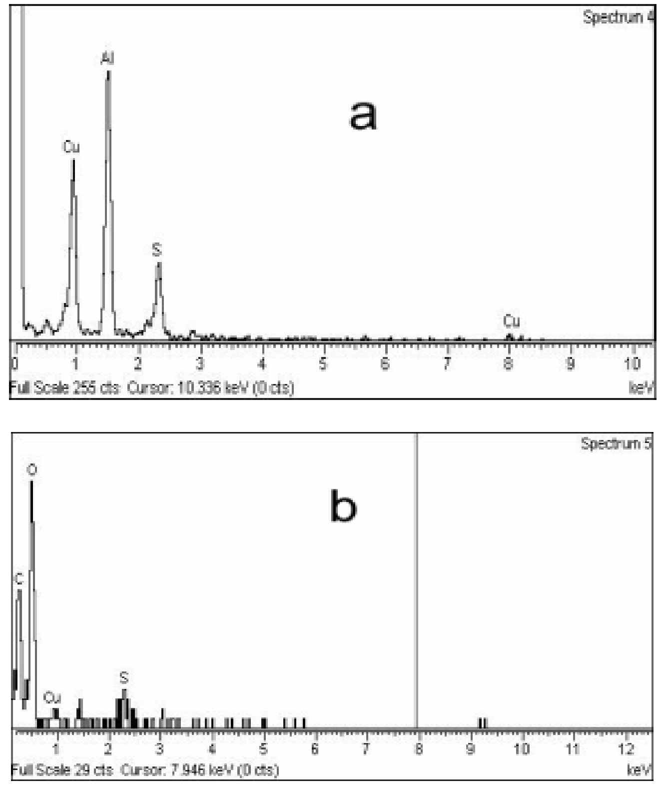

Fig. 5: EDAX Compositional analysis of CuS/glucose of a.Cu/S = 3:2 & b. Cu/S = 2:3.

60^o centigrade to evaporate the solvent (and the medium). Two typical EDAX spectra of as deposited CuS(Cu:S=2:3 , 3:2) have been shown in Fig.5. The analysis shows that the ratios of atomic % of copper and sulphur are closely in agreement with those of Cu/S volumetric ratios.

4. CONCLUSION

A simple method for the synthesis of CuS nanoparticles by a chemical route was presented. The method was nontoxic, environment friendly and low cost. The capping materials played important role in controlling their morphologies as well as in confinement of nanoparticles. Thiourea was used as sulphur source because release of S^{2-} ions from thiourea in aqueous ammonia can be controlled by adjusting the pH value of the reaction. The XRD measurement showed both chalcocite and covellite phase of CuS superimposed on the matrix materials. HRTEM morphology exhibits spindle type nanoparticles and well defined nanorods depending on the bath parameters. The optical properties of the CuS nanoparticles exhibited good blue shift of absorption edge with enhancement of band gap to 3-3.4 eV as well as high photoluminescence intensity with a uniform distribution of well defined nanoparticles. The glucose capped CuS exhibits a spectacular enhancement of PL intensity compared to that of CuS/starch. The Cu/S volumetric ratio was also confirmed from the compositional analysis of EDAX. Hence, it is inferred from the experiment that sulphur can induce a good UV emission in copper sulphide which can be exploited for fabrication of efficient UV-emitter & other photovoltaic devices.

5. ACKNOWLEDGMENTS

We must thank the University Grant Commission, North Eastern Regional Office, Guwahati, Assam for the financial support in part in carrying out this research work.

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