Chemical Synthesis of Copper Sulphide nanoparticles embedded in PVA matrix

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Received 28 June 2012; accepted 14 July 2012

Abstract

Thin films of copper sulphide nanoparticles were deposited on glass substrates at room temperature 303K to 363K through chemical route. Equi-volume and equimolar 0.01M solution of copper acetate and thiourea was used for the synthesis in an alkali medium. The X-ray diffraction showed both the covellite and the chalcocite phase of copper sulphides with hexagonal & orthorhombic crystal structure respectively. The formation of nanoparticles was confirmed by UV-visible absorption and PL measurements which showed an enhancement of band gap. The HRTEM images exhibited the spherical size of nanoparticles varied from 20nm at room temperature to200nm at high temperature growth. The PL spectra showed the identical blue-green emission irrespective of growth temperature.

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Key words: Chemical synthesis, CuS/Cu₃S, PVA, Quantum confinement

1. Introduction

Nanostructures materials have attracted a great deal of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. Owing to quantum size effects and surface effects [1-4], nanoparticles can display novel optical, electrical, magnetic, chemical and structural properties that might find important technological applications. Copper sulphide has fairly complex crystal chemistry owing to its ability to form sub-stoichiometric compounds Cu₅S (2≥x≥1) [5]. CuS phase exists in two forms, the amorphous brown chalcocite CuS and green crystalline covellite [6]. Cu₅S has many forms in bulk at room temperature. They are chalcocite (orthorhombic CuS), djurleite (mono-clinic-prismatic Cu₁₀S) etc. [7, 8]. In the chalcocite group, Cu₁₅S (0≤x≤0.6), eight compounds exist. They are γ-chalcocite Cu₅S (low, orthorhombic), β-chalcocite Cu₅S (high, hexagonal), djurleite Cu₁₅S, digenite Cu₁₀S, roxbyite Cu₁₅S, anilite Cu₁₅S, geerite Cu₁₆S and spionkopite Cu₁₆S. While γ-chalcocite, djurleite and anilite form low temperature phases, the tetragonal Cu₁₉S phase, low digenite, Cu₁₈S and roxbyite, Cu₁₅S form metastable phases [9]. As CuS is a P-type material, it has a wide scope in photovoltaic device application such as solar cells. Its band gap is 1.27eV. So in this nano-region CuS may exhibit its expected to stabilize copper sulphide particles. The as formed copper (1) ions, then have the probability to

2. Experimental

2.1 Synthesis

Thin films of CuS nanoparticles were deposited on glass substrates by reacting copper acetate monohydrate (Cu (ac)₂) with thiourea (H₂NCSNH₂) in the presence of polyvinyl alcohol (PVA) as capping agents. A 3% PVA solution was mixed with copper acetate solution to act as capping agent. Equi-volume and equimolar 0.01M solution of copper acetate and thiourea were used for the synthesis. Ammonia was added to the PVA mixed copper acetate solution to make copper ion complex where thiourea solution was added drop wise for the formation of final copper sulphide matrix solution. The synthesized copper sulfide solution became greenish in colour. The reaction mechanism can be given as follows-

\[\begin{align*}
\text{Cu}^{2+} + 4\text{NH}_3 & \leftrightarrow \text{Cu} (\text{NH}_3)^2+ \\
\text{NH}_3 + \text{H}_2\text{O} & \leftrightarrow \text{NH}_4^+ + \text{OH} \\
(\text{NH}_3)\text{CS} + 2\text{OH}^- & \leftrightarrow \text{S}^2- + 2\text{H}_2\text{O} + \text{H}_2\text{CN}_2 \\
\text{Cu}^{2+} + \text{S}_2 & \leftrightarrow \text{CuS(s)}
\end{align*}\]

However copper (2) ions can readily be reduced to copper (1) ions by thiourea. The PVA in the reaction solution is expected to stabilize copper sulphide particles. The as formed copper (1) ions, then have the probability to
combine with sulphide ions to form chalcocite particles (Cu$_2$S) as follows:

$$2 \text{Cu}^{2+} + 2(\text{NH}_3)\text{CS} \leftrightarrow 2\text{Cu}^+ + (\text{NH}_3)_2 \text{S}_2 \text{Cu}_2\text{S}_2 + 2\text{H}^+$$

2Cu$^+$ + S$^2$ $\rightarrow$ Cu$_2$S

The glass substrates were cleaned and these were dipped to cast thin films. The films were taken for XRD (X-ray diffraction) and the filtrate solution for other optical measurements. In the present study, the growth temperature was increased from 303K (Sample1:S1) to 363K (Sample2: S2).

2.2 Characterization

The structural characterization was done by X-ray diffraction technique and transmission electron microscopy (TEM). The X-ray diffractograms were recorded using copper Kα radiation. The tube was operated at 20kV 30mA. The 2θ varied from 15° to 70° with scanning rate (0.05°). The TEM morphology was recorded using JEM 2100 (Jeol Electronic Microscope) at accelerating voltage 200kV and beam current 102μA. The optical spectra of nanoparticle were measured using USB-2000 UV-visible spectrometer over the range 300nm to 700nm. The PL spectra were also recorded in the wavelength range 350nm to 700nm. The atomic absorption was recorded by Atomic absorption spectrometer (Perkin Elemer 3110).

3. Results and discussion

3.1 Structural characterization

Copper sulphide nanoparticles were prepared through the reaction of copper acetate and thiourea as discussed in experimental details. Different sizes of nanoparticles were obtained with respect to the growth of temperature. The XRD pattern of deposited copper sulphide exhibited weak diffraction peaks superimposed on PVA matrix (Fig.1). The diffraction peaks at 19.5° and 24° corresponding to (101) and (200) planes were corresponding to PVA. This type of weak diffraction peaks were reported by other workers particularly when the sample is embedded in a polymer matrix like PVA and PNIAP (poly N-isopropyl lacrylamide) [12, 13, 22]. The XRD showed prominent (102), (103) and (110) planes of CuS covellite phase corresponding to 2θ at 44°, 57°, 53°.85°. The other prime peaks at 23.9°, 26.5°, 30.65° and 32.95° were corresponding to (016), (046), (400) and (412) planes of chalcocite (Cu$_2$S). This was confirmed from standard JCPS data no.2-1272 for covellite (hexagonal) and chalcocite copper sulphide with orthorhombic phase respectively [14, 15]. Cu$_2$S had tendency to form chalcocite orthorhombic type crystal at room temperature as reported by other workers [14]. The natures of diffraction pattern of PVA capped copper sulphide at room temperature303K and at elevated temperature (363K) were quite identical. However, the prominence of Cu$_2$S peaks at high temperature indicated an increase in overall particle size. The formation of Cu$_2$S was also supported by atomic absorption measurements where the concentration of copper increased at high temperature (Table1). The HRTEM showed the shape and size of particles formed in the samples which were of mainly spherical type (Fig.2). Most of the other workers also found spherical and hexagonal copper sulphide particles. The average individual particle size deposited at room temperature was around 10-20nm whereas it got agglomerism to form overall size up to 200nm at high temperature. Similar type of TEM morphology was also found in chitosan capped copper sulphide [10]. TEM morphology clearly indicated that PVA had acted as a good stabilizer where the particles were nicely embedded irrespective of growth temperature.

3.2 Optical characterization

The absorption spectra of sample (S1) and sample (S2) synthesized at 303K and 363K were shown in Fig. 3a and Fig.3b respectively. The UV-visible measurements exhibited an absorption peak at 364nm and a shoulder around 629nm for copper sulphide synthesized at room temperature Fig.3a. This broad absorption suggested covellite phase [10, 16] of copper sulphide which is blue shifted because of quantum confinement from its bulk in IR region. The short wavelength side peak corresponds to that of chalcocite phase [5]. The existence of chalcocite Cu$_2$S in chemically bath deposited samples was also revealed by other workers [5, 11]. Haram, et al [17] found absorption at 475nm corresponding to chalcocite phase. F Li, et al [11] found absorption at 314nm and 601nm. Cu$_2$S had mainly stable phases with varied stoichiometry because of effect of 3d electrons. On increasing the growth temperature, shorter wavelength peak red shifted to 381nm whereas the other is blue shifted to 601nm. This clearly indicated the presence of both CuS and Cu$_2$S in the prepared samples. Similar simultaneous red and blue shifts on temperature refluxing in short and long wavelength region were reported by Boey et al [10]. They found broad absorbance at near IR region at 1025nm, characteristic of covellite CuS and that of absorbance at 475nm due to chalcocite Cu$_2$S in chitosan capped copper sulphide. Hence it could have been been inferred that like chitosan the PVA could act as a reducing agent besides being a stabilizer or protecting agent. Some noise absorption was also observed around 364nm in the short wavelength side for room temperature grown copper sulphide. This might be due to the surface oxidation of chalcocite under aqueous and ambient atmosphere. Chalcocite reacted with air and developed CuSO$_4$ surface phase in addition to cuprite (Cu$_2$O) and tenorite (CuO) [18].

![Fig.1. XRD patterns of Copper Sulphides nanoparticles](image-url)
Fig. 2. TEM images of Copper Sulphides (S1: a, b) & (S2: c, d)

Fig. 3. UV-visible absorption spectrum of CuS nanoparticles (S1: a) & (S2: b)

Fig. 4. PL spectra for Copper Sulphides nanoparticles for samples S1 & S2
3.3 PL spectroscopy
Fluorescence spectroscopy is a kind of electromagnetic spectroscopy which analyses fluorescence from a sample. It involves using a beam of light, usually UV light that excites the electrons in the molecules of certain compounds and causes them to emit light of a lower energy, typically but not necessarily visible light. Photoluminescence of those two CuS samples at room temperature and high temperature are shown in Fig. 4a and 4b. The PL spectra was taken using excitation wavelength 325nm. The figures show inhomogeneous broadening of emission. In Sample (S2), PL peaks occur at 360nm, 396nm, 468nm and a broad shoulder at extreme blue region. A close observation indicates the presence of some weak blue-green emission at 451nm, 482nm, and 493nm. Similar results are found for Sample (1) at 362nm, 396nm, 468nm and 600nm. Weak peaks are found at 432nm and 474nm. The PL intensity increases with the rise of deposition temperature. Similar PL observations were also reported by other workers [18, 19, 20]. Blue emission was owing to the spherical copper sulphides [11, 21].

4. Conclusion
The copper sulfide nanoparticles can be prepared through simple chemical route. PVA was found to play a key role in the confinement as well as in stabilization process. The XRD confirms the formation of copper sulphides embedded in PVA by showing the diffraction peaks of the corresponding materials. Copper sulphides exhibit both covellite and orthorhombic chalcocite phase irrespective of growth temperature. This is supported by UV-visible measurements which show chalcocite CuS absorbance at 364nm and covellite CuS at 629nm. In increasing the growth temperature, the short wavelength absorption is red shifted whereas the long wavelength absorption is blue shifted. This is in well agreement with the reported results. The PL measurements show blue-green emission for both the copper sulphide samples which confirms the spherical shape of CuS particles.

5. Acknowledgement
The authors thank the Chemistry Department, Gauhati University, Guwahati, SAIF, NEHU, Shillong and IIT, Guwahati for carrying out this research work.

References

Source of support: Nil; Conflict of interest: None declared