

A simple synthesis and characterization of CuS nanocrystals

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Abstract. Water-soluble CuS nanocrystals and nanorods were prepared by reacting copper acetate with thioacetamide in the presence of different surfactants and capping agents. The size of the nanocrystals varied from 3–20 nm depending on the reaction parameters such as concentration, temperature, solvent and the capping agents. The formation of nanocrystals was studied by using UV-visible absorption spectroscopy.

Keywords. Copper sulfide; nanocrystals; solution synthesis.

1. Introduction

Synthesis and characterization of nanocrystals of semi-conducting metal sulfides have been an intense field of research due to their interesting properties and potential applications (Murray *et al* 2000; Hu *et al* 2001; Trindade *et al* 2001; Rao *et al* 2004; Rotello 2004). For example, when the size of the nanocrystals is smaller than the Bohr excitation radius of the material, they exhibit properties which are size dependent and distinct from the bulk (Alivisatos 1996). Such materials are promising candidates in electronics, data storage, energy storage, catalysis and sensors (Heath *et al* 1998; Huynh *et al* 2002; Kung and Kung 2004). It is, therefore, important to develop synthetic strategies which are simple, cost-effective, environment friendly, easily scalable and at the same time with parameters to control size and shape of the materials. CuS has potential applications in solar cells, IR detectors and lubrication (Mane and Lokhande 2000). It exhibits fast-ion conduction at high temperature (Paul *et al* 1993). However, copper sulfide has a fairly complex crystal chemistry owing to its ability to form sub-stoichiometric compounds, Cu_xS ($2 \geq x \geq 1$) (Evans 1971, 1979; Grijavala *et al* 1996). The CuS phase exists in two forms, the amorphous brown CuS and the green crystalline covellite (Brelle *et al* 2000). Traditionally CuS is prepared by solid state reactions (Parkin 1996). There are a few reports of solution synthesis as well (Silvester *et al* 1991; Haram *et al* 1996; Henshaw *et al* 1997; Jiang *et al* 2000; Dong *et al* 2002; Wang *et al* 2002; Lu *et al* 2003; Zhang *et al* 2004). Jiang and coworkers (2000) prepared nanocrystalline Cu_9S_8 , Cu_7S_4 and CuS solvothermally by controlling the release of S^{2-} from thiourea. Dong *et al* (2002) used water-in-carbon dioxide micro-emulsion to prepare CuS nanocrystals.

Others involve micro-emulsion synthesis using non-ionic Tritin X100 surfactant, sonochemical technique and elemental reactions in liquid ammonia (Haram *et al* 1996; Henshaw *et al* 1997; Wang *et al* 2002). Silvester and coworkers (1991) investigated the kinetics of formation of Cu_xS from Cu^{2+} salt and H_2S gas in detail. Nanorods of CuS have also been prepared by using liquid-crystal templates (Lu *et al* 2003). Notably, Larsen *et al* (2003) reported a solventless synthesis of Cu_2S nanorods, by heating copper thiolate to high temperatures. Recently, we have obtained single crystalline ultra-thin films of CuS prepared by a novel technique involving reactions at the liquid-liquid interface (Gautam *et al* 2004). However, in view of its usefulness, there is a need to evolve environmentally friendly routes to prepare CuS nanocrystals, which yields nanocrystals of desired sizes in a controllable manner.

In this article, we describe a facile aqueous synthesis of CuS nanocrystals of various sizes and shapes. The effects of various reaction parameters on the size of the nanoparticles have been examined. Use of surfactants renders stability to the nanocrystals for months against ambient oxidation and corrosion. Importantly, the present strategy avoids toxic chemicals either in the form of reactants or as side products.

2. Experimental

Copper acetate monohydrate ($\text{Cu}(\text{ac})_2$) and thioacetamide (CH_3CSNH_2) were used as Cu and sulfur sources, respectively for all the reactions. In a typical preparation, 0.0050 g of $\text{Cu}(\text{ac})_2$ (25 μmol) was dissolved in 10 ml deionized water. In another container, 0.0020 g of thioacetamide (25 μmol) and 0.200 g of sodium-*bis*(2-ethylhexyl) sulfosuccinate (Na-AOT) were dissolved in 10 ml of deionized water. The $\text{Cu}(\text{ac})_2$ solution was added to the thioacetamide solution dropwise at 30°C with continuous stirring

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over a period of 20 min. The solution turned golden brown as soon as the first drop of $\text{Cu}(\text{ac})_2$ solution was added and the colour deepened with more addition. The brown solution turned green over a period of 12 h. Cetyl trimethylammonium bromide (CTAB) capped nanocrystals were prepared in a similar fashion, using 0.100 g of CTAB instead of Na-AOT. Similarly, polyvinyl pyrrolidone (PVP) capped nanocrystals were prepared in methanol medium instead of water, keeping all other conditions identical. The green solutions containing CuS nanocrystals were examined by transmission electron microscopy (TEM), electronic absorption spectroscopy and X-ray diffraction technique. A drop of the solution was dried on a holey carbon grid and investigated using a JEOL (JEM3010) transmission electron microscope operating with an accelerating voltage of 300 kV. The solution was dried on a glass slide in order to record the X-ray diffraction pattern on a Siemens 5005 Diffractometer with reflection Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). UV-vis absorption spectra of the nanocrystals in water were recorded using a Perkin-Elmer UV-visible spectrometer.

3. Results and discussion

In figure 1a, we show a typical TEM image of 11 nm CuS nanocrystals obtained by reacting 1.25 mmolar solution, $\text{Cu}(\text{ac})_2$, with 1.25 mmolar solution of thioacetamide. The histogram in the inset shows the particle size distribution. The nanocrystals are not perfectly spherical and the particle size indicates average of the horizontal and vertical diameters. The nanocrystals are stable in solution for long periods, due to surface passivation by the surfactant and do not precipitate even after months. However, the TEM images reveal that the particles tend to agglomerate to some extent. This is probably due to the drying artifact during the preparation of the grid for TEM imaging. The top inset in figure 1a shows the selected area diffraction pattern (SAED) of the nanocrystals. The pattern can be indexed on hexagonal CuS. In figure 2a, we show the X-ray diffraction pattern of the 11 nm nanocrystals obtained at 30°C. All the peaks in the pattern correspond to phase pure CuS in the space group $P6_3/mmc$ (JCPDF no. 03-0724). Figure 2b shows electronic absorption spectrum of the

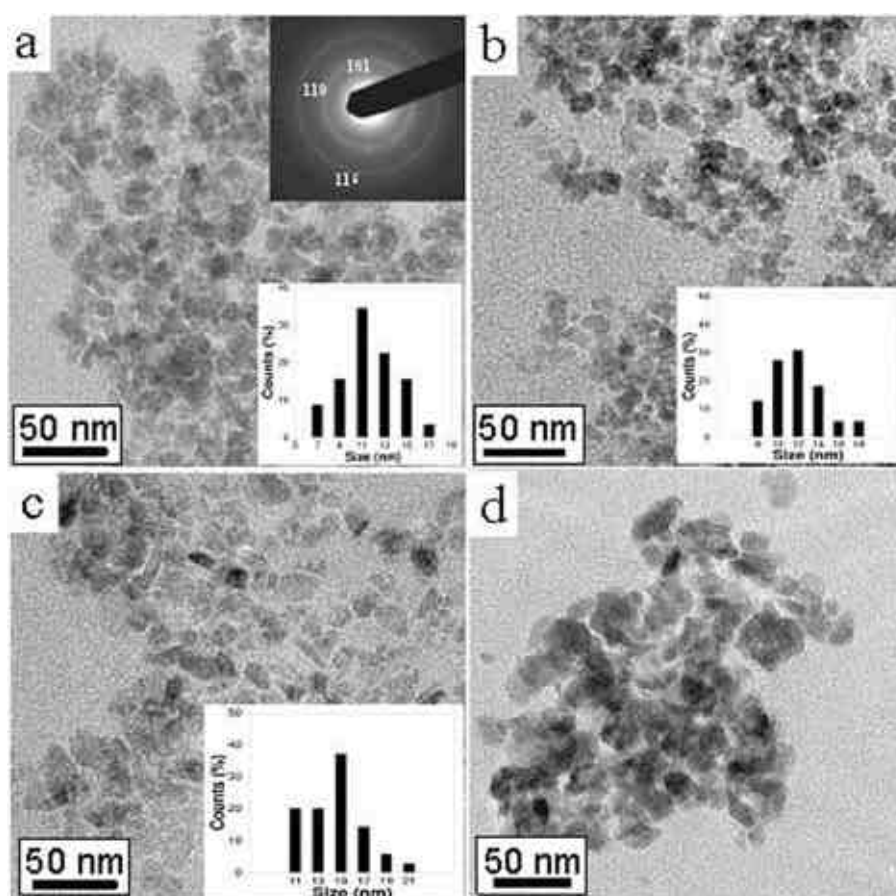


Figure 1. TEM images of the CuS nanocrystals obtained by using **a.** 12.5 μmol of $\text{Cu}(\text{ac})_2$ (11 nm), **b.** 25 μmol of $\text{Cu}(\text{ac})_2$ (12 nm), **c.** 37.5 μmol of $\text{Cu}(\text{ac})_2$ (15 nm) and **d.** reaction temperature of 15°C (20 nm).

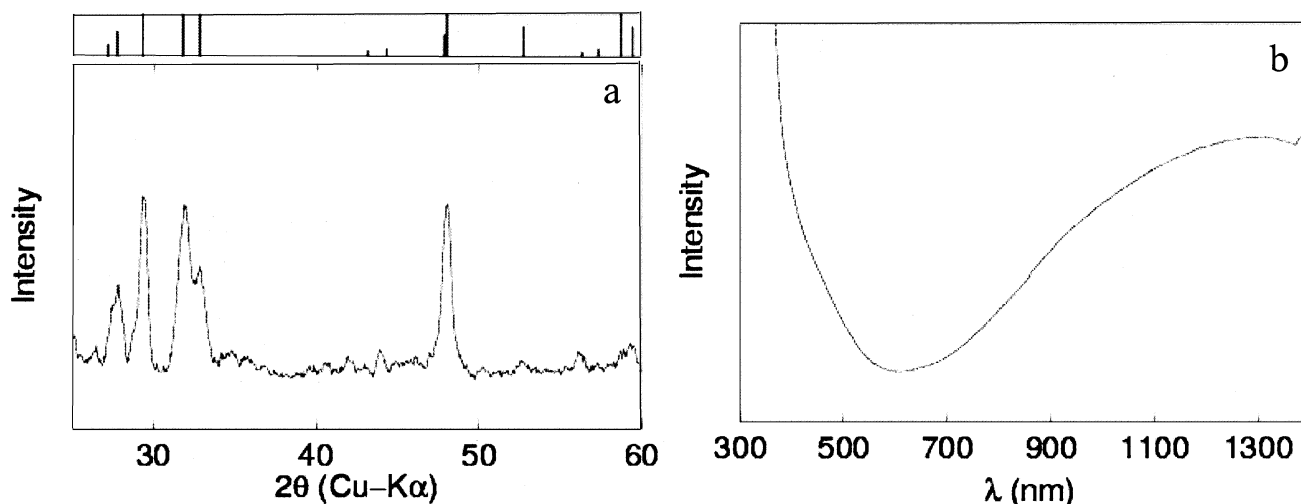


Figure 2. a. The XRD pattern of 11 nm CuS nanocrystals. The upper panel shows the expected peak positions and b. the corresponding UV-vis absorption spectrum of the nanocrystals.

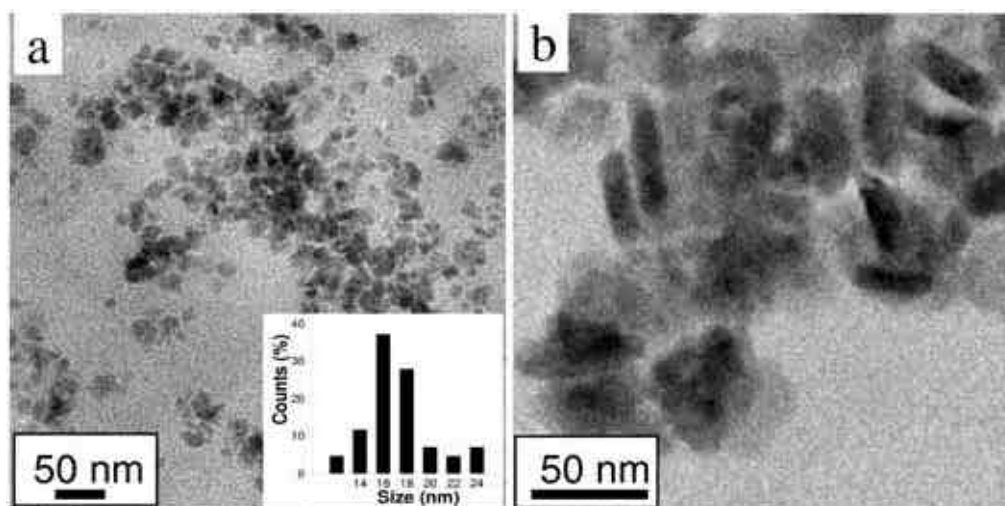


Figure 3. a. 16 nm CuS nanocrystals obtained reducing the amount of NaAOT by half and b. CuS nanorods obtained in presence of excess NaAOT.

nanocrystals. Eventhough Cu_xS has many stable phases with varied stoichiometry, each phase has its distinct optical absorption spectrum. The broad absorption in the near IR region corresponds to the pure covellite phase (Silvester *et al* 1991; Yumashev *et al* 1996). We do not observe any shoulder at ~ 450 nm corresponding to the Cu_2S phase (Haram *et al* 1996).

The particle size of CuS increases with the reactant concentrations. For example, 12 nm and 15 nm nanocrystals were observed by increasing the concentrations of all the reactants two-fold and four-fold, respectively (figures 1b and c). The size of the nanocrystals is also dependent on the reaction temperature. We obtained larger nanocrystals of ~ 20 nm (compared with the 12 nm particles) with a broad size distribution by carrying out the preparation at

15°C (see figure 1d). However, the product obtained at 50°C had large agglomerates of 8–12 nm nanocrystals. Fast production of a large number of nuclei at 50°C appears to result in smaller nanocrystals which get attached to one another due to high temperature.

The concentration of Na–AOT influences size and shape of the CuS nanocrystals. We obtained 16 nm nanocrystals of CuS (figure 3a) by using 0.100 g of the surfactant as compared to the 12 nm nanocrystals obtained by using 0.200 g as shown in figure 1a. By increasing the amount of Na-AOT to 0.300 g, rod shaped CuS nanocrystals were obtained as shown in figure 3b.

CuS nanocrystals of much smaller diameter were obtained by using methanol solvent along with PVP cap and CTAB cap in the aqueous medium. Figure 4a displays the

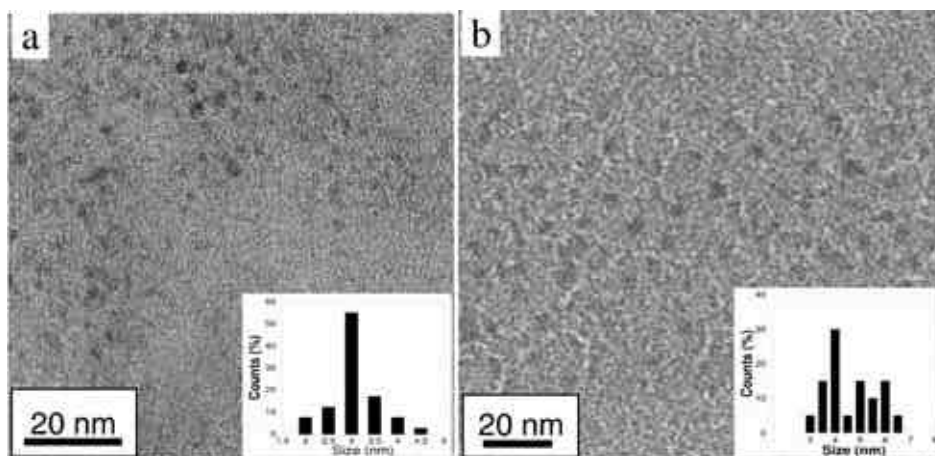


Figure 4. a. 3 nm CuS nanocrystals obtained in methanol solvent and b. 4 nm CuS nanocrystals obtained in an aqueous synthesis when CTAB was used as capping agent in aqueous medium.

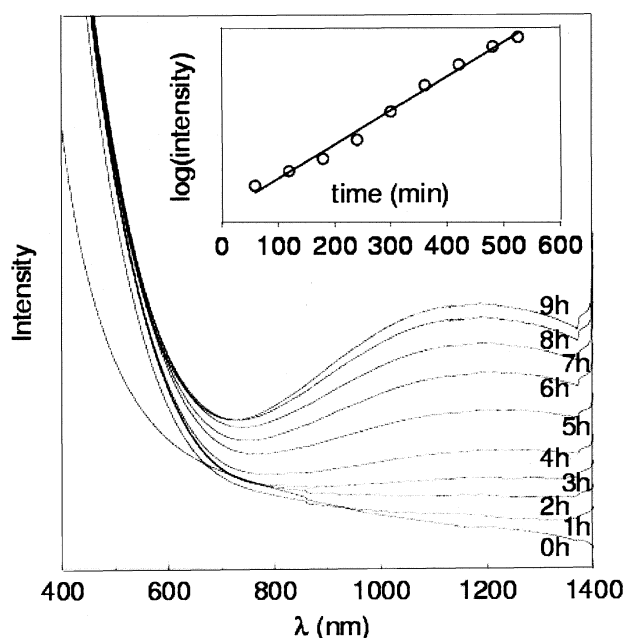


Figure 5. The UV-vis absorption spectra of the CuS nanocrystals recorded at 1 h interval as they form. The inset shows the log of intensity of near-IR absorption band vs time of the reaction.

3 nm CuS nanocrystals obtained thus in methanol solvent, keeping concentrations of all the chemicals same as the sample shown in figure 1b. Part of the nanocrystals precipitated out, the rest remaining in the solution imparting green colour. Figure 4b shows 4 nm CuS nanocrystals obtained by using 0.10 g of CTAB.

The kinetics of formation of CuS nanocrystals have been reported by Silvester *et al* (1991), who employed gaseous H_2S as one of the reactants. We now examine the growth of nanocrystals, keeping all the reactants in solution

phase. The near IR absorption band in the absorption spectra of CuS nanocrystals provides a good means to study the growth process. This is because the band does not shift with time and its intensity is directly proportional to the amount of CuS in the solution. In figure 5 we show the UV-vis spectra of the CuS nanocrystals (for the sample in figure 1b) recorded at intervals of 1 h. As can be seen, the band is absent when the two solutions are just mixed and gradually grows with time. The inset in the figure displays the plot of log of intensity of the band against time showing a near linear growth of the band.

4. Conclusions

We have prepared CuS nanocrystals of various sizes and shapes by a simple and environmentally benign technique involving the reaction of copper acetate with thioacetamide. The reaction carried out in polar organic solvent in presence of CTAB yielded 3–4 nm nanocrystals while that in aqueous medium yielded 11–20 nm nanocrystals. The technique is cost-effective and scalable.

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