

Synthesis of TOPO-capped Nanocrystals of Copper Sulphide from a Single-source Precursor, [Cu(S₂CNMe(ⁿHex))₂]

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Received 10 July 2002; revised 15 March 2002; accepted 5 April 2004.

ABSTRACT

Nearly mono-dispersed TOPO-capped copper sulphide nanocrystals of *ca.* 4.5 nm (diameter) have been synthesized from [Cu(S₂CNMe(ⁿHex))₂]. The absorption spectrum of the (Cu₂S) nanoparticles shows a large blue shift (2.09 eV) in relation to bulk Cu₂S (1022 nm, 1.21 eV). The PL gives a broad spectrum with an emission maximum at 477 nm. The HRTEM of the nanoparticles shows clusters of particles on the copper grid with clear lattice fringes.

KEYWORDS

Nanocrystals, copper(I) sulphide, TOPO, photoluminescence, TEM, SAED.

1. Introduction

Copper sulphide is a potentially cheap and less hazardous material than CdS, CdSe and PbS but has received scant attention. The synthesis of copper sulphide has been achieved from aqueous sols,¹ monolayers,² bilayer lipid membranes,^{3,4} LB films,⁵ and water-in-oil (w/o) micro-emulsions of bis(2-ethyl-hexyl)sulphosuccinate sodium salt.⁶ In all reports except in the case of aqueous sols, the particles have been poorly characterized. Haram *et al.*⁷ reported the synthesis of copper sulphide nanoparticles by reacting a copper ammonia complex with an equimolar thiourea solution in Triton-X 100 water-in-oil microemulsions. They observed a sharp blue-shifted peak at 475 nm in the UV/Vis spectrum and by using this, the formation of the chalcocite (Cu₂S) phase was inferred. In this paper we report the synthesis of copper sulphide nanoparticles using a single-source route as previously described for CdS and CdSe nanoparticles.⁸

2. Experimental

2.1. Chemicals

Tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylphosphine (TOP), carbon disulphide, copper sulphate and *N*-methylhexylamine were purchased from Aldrich Chemical Company Ltd. and 1,4-dioxane, methanol and toluene from BDH. TOPO was purified by vacuum distillation at *ca.* 250°C (0.1 Torr). The solvents were distilled, deoxygenated under a nitrogen flow and stored over molecular sieves (type 4 Å, BDH) before use.

2.2. Preparation of Cu(S₂CNMeHex)₂

The single-source precursor [Cu(S₂CNMeHex)₂] was prepared by the reaction of *N*-methylhexylamine (3.50 g, 30.4 mmol) and carbon disulphide (1.34 g, 30.4 mmol) in dioxane (30 mL) at 0°C in the presence of a sodium hydroxide (1.22 g, 30.4 mmol) solution in water (30 mL). The solution was stirred for 15 min at 0°C and then 10 min at room temperature. Copper sulphate (2.43 g, 15.02 mmol) in water (40 mL) was then added drop-wise while

stirring. A black precipitate was formed which was filtered, washed with water and dried under vacuum.

2.3 Preparation of Cu₂S Quantum Dots

The method used is a modification of the method described by Trindade and O'Brien.^{9,10} [Cu(S₂CNMe(ⁿHex))₂] (1.0 g) was dissolved in TOP (15 mL) and injected into hot TOPO (20 g). A decrease in temperature of 20–30°C was observed. The solution was then allowed to stabilize at 200°C and heated for 15 min at this temperature. The pale yellow solution was cooled to approximately 70°C. A black material (0.65 g) settled in the flask and was separated by decanting the yellow solution. On addition of an excess of methanol to the yellow solution a thin precipitate formed. The precipitate was separated by centrifuge and redispersed in toluene.

2.4. Instrumentation

2.4.1. UV/VIS Absorption Spectroscopy

A Philips PU 8710 spectrophotometer was used to carry out the optical measurements of the semiconductor nanoparticles. The samples were placed in silica cuvettes (1 cm path length).

2.4.2. Photoluminescence Spectroscopy

A Spex FluoroMax instrument with a xenon lamp (150 W) and a 152 P photomultiplier tube as a detector was used to measure the photoluminescence of the particles. The samples were quantitatively prepared by dissolving 25 mg in 10 mL toluene. The wavelength of excitation was set at a lower value than onset of absorption of a particular sample.

2.4.3. X-Ray Diffraction (XRD)

X-ray diffraction patterns were measured on a Philips PW 1700 series automated powder diffractometer using Cu-K_α (radiation at 40 kV/40 mA with a secondary graphite crystal monochromator. Samples were prepared on glass slides (5 cm).

2.4.4. Electron Microscopy

A Joel 2000 FX MK 1 electron microscope, operated at 200 KV,

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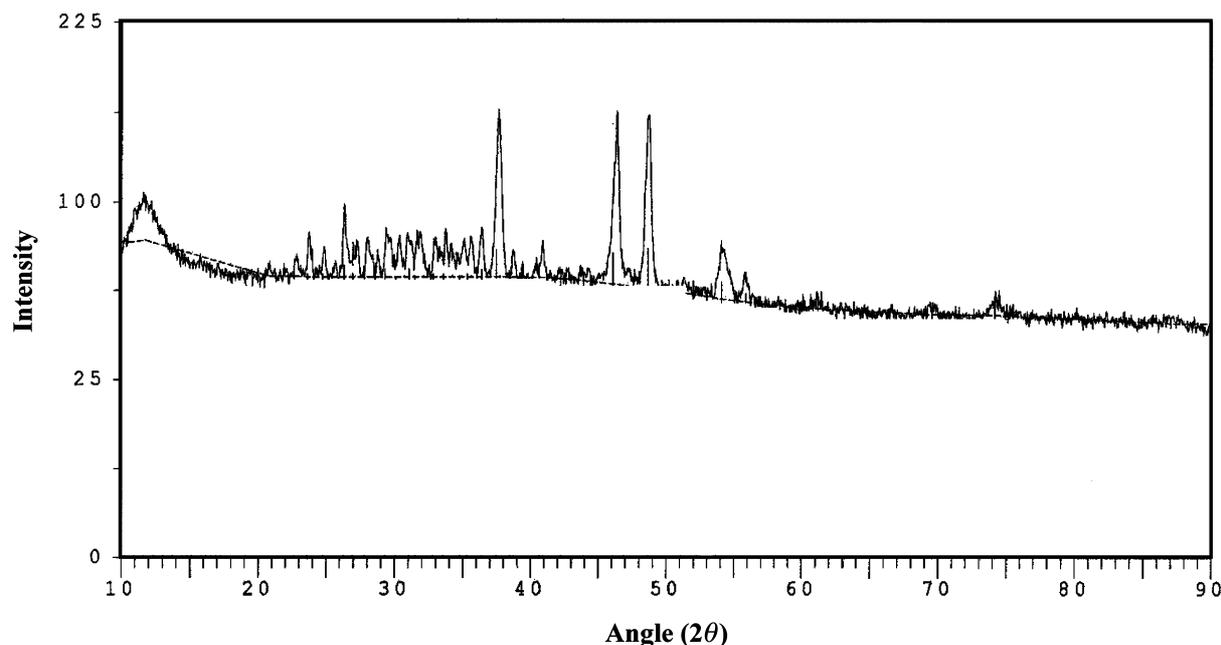


Figure 1 XRD pattern of bulk Cu_2S synthesized at 250°C .

with an Oxford Instrument AN 10000 EDS Analyser was used for the conventional TEM (transmission electron microscopy) images. Selected-area electron diffraction (SAED) patterns were obtained using a Jeol 2000FX MK 2 electron microscope, operated at 200 kV. The samples for TEM and SAED were prepared by placing a drop of a dilute solution of sample in toluene on a copper grid (400 mesh, agar). The excess solvent was wicked away with a paper tip and completely dried at room temperature.

3. Results and Discussion

Thermolysis of $[\text{Cu}(\text{S}_2\text{CNMe}(\text{Hex}))_2]$ in TOPO gave a comparatively low yield of copper sulphide nanocrystals at 250°C since the bulk of the precursor decomposed to give a black residue which settled in the reaction flask. Analysis of the residue by XRD (Fig. 1) showed it to be a bulk monoclinic Cu_2S (Table 1). The growth experiment was then repeated at lower temperatures (180°C , 200°C) and shorter times (15 min) in the view that the conditions might have been too vigorous, causing the precursor to decompose into bulk copper sulphide. No growth of any kind occurred at 180°C , but a comparatively better yield was obtained at 200°C although again a substantial amount of precursor decomposing to bulk copper sulphide.

3.1. Optical Properties

Copper sulphide has many stable phases including chalcocite (Cu_2S) and the sulphur-rich covellite (CuS).⁷ Each stable phase has its own characteristic optical property, e.g. covellite (CuS) has a characteristic broad absorption band in the near IR region (*ca.* 920 nm). This absorption is completely absent in the chalcocite (Cu_2S) phase. In this work the absorption spectrum of the (Cu_2S) nanoparticles shows a feature at 376 nm (3.30 eV) with the absorption edge set at 430 nm (3.75 eV), and a large blue shift (2.09 eV) in relation to bulk Cu_2S (1022 nm, 1.21 eV) (Fig. 2). The absence of any absorption in the near-IR (*ca.* 920 nm) region infers that the phase of copper sulphide is Cu_2S (chalcocite) rather than CuS (covellite). The sharp band edge could be assigned to the S_0 to S_1 molecular transition as reported previously.⁷ The PL spectrum shows a relatively broad emission spectrum, with a maximum at 477 nm.

Table 1 XRD data for the black residue obtained after thermolysis (bulk monoclinic Cu_2S)

d/Å Exp	d/Å Lit (%int)	d/Å Exp (% int)	d/Å Lit(% int) (%int)
3.91 (10)	3.93 (5)	2.40 (96)	2.40 (70)
3.75 (22)	3.77 (10)	2.33 (13)	2.34 (5)
3.59 (15)	3.60 (10)	2.21 (17)	2.22 (20)
3.39 (38)	3.39 (30)	2.06 (3)	2.06 (10)
3.31 (16)	3.31 (10)	1.96 (100)	1.96 (80)
3.20 (18)	3.21 (20)	1.87 (97)	1.87 (100)
3.05 (21)	3.05 (20)	1.78 (4)	1.78 (5)
2.95 (18)	2.97 (5)	1.69 (27)	1.69 (40)
2.89 (21)	2.84 (5)	1.64 (12)	1.64 (20)
2.84 (21)	2.84 (5)	1.51 (4)	1.51 (20)
2.73 (15)	2.73 (10)	1.35 (3)	1.35 (10)
2.66 (24)	2.67 (10)	1.27 (8)	1.27 (30)
2.56 (17)	2.58 (5)	1.11 (2)	1.11 (10)
2.53 (17)	2.54 (10)		
2.47 (21)	2.47 (20)		

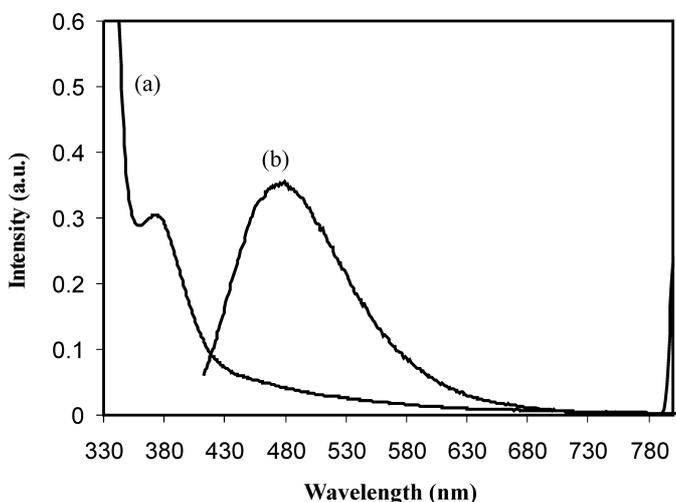


Figure 2 Cu_2S nanoparticles: a, absorption band edge at 430 nm; b, emission maximum at 477 nm.

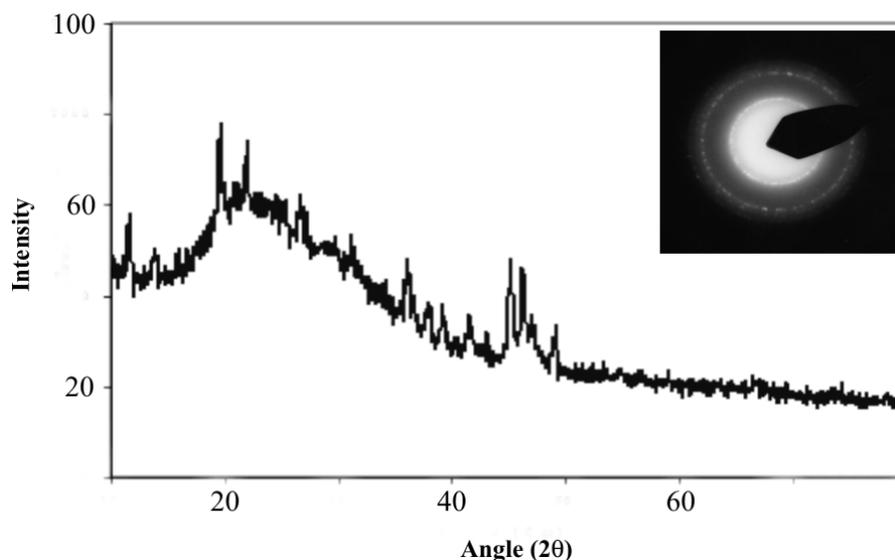


Figure 3 XRD and SAED pattern of Cu_2S nanoparticles.

Table 2 XRD data for nanoparticulate Cu_2S .

d/Å Exp	Int. (%)	d/Å Exp	Int. (%)
7.37	60	2.48	52
6.32	32	2.36	25
4.44	27	2.16	30
4.02	59	2.00	100
3.32	28	1.96	86
2.85	25	1.93	46
2.62	21	1.86	35
2.56	17	1.68	6

3.2. Structural Characteristics

Cu_2S has been reported to have three possible crystal structures i.e. hexagonal, monoclinic and tetragonal, consistent with the mineral names: high chalcocite, low chalcocite and tetragonal chalcocite.¹¹ The poorly resolved XRD and SAED patterns suggest that the nanoparticles have the composition Cu_2S . The pattern is shown in Fig. 3 and the data are given in Table 2. The diffuse diffraction rings of the SAED pattern (Fig. 3) are indicative of their nanoparticulate size. The TEM micrograph of

the Cu_2S nanoparticles shows particles that form clusters on the copper grid (Fig. 4a). The particle size is in the range of ca. 3–5 nm. Accurate size determination from the TEM image is difficult due to clustering. The HRTEM image (Fig. 4b) more clearly shows this clustering of particles but with clear lattice fringes. The EDAX spectrum shows the presence of copper and sulphur, with a strong peak for phosphorus due to TOPO.

4. Conclusion

Copper sulphide nanocrystals of ca. 2.5 nm (diameter) were synthesized from $[\text{Cu}(\text{S}_2\text{CNMe}(\text{Hex}))_2]$. The absorption spectrum shows a large blue shift (2.09 eV) in relation to bulk Cu_2S (1022 nm, 1.21 eV). The absence of any absorption in the near IR (ca. 920 nm) region indicates the composition of copper sulphide to be Cu_2S (chalcocite) rather than CuS (covellite). The photoluminescence spectrum gives a relatively broad emission spectrum with the emission maximum at 477 nm, while the EDAX spectrum shows the presence of copper and sulphur, with a strong peak for phosphorus due to TOPO. The TEM micrograph of the Cu_2S nanoparticles shows clusters of particles on the copper grid and the SAED pattern of the Cu_2S nanoparticles has diffuse diffraction rings.

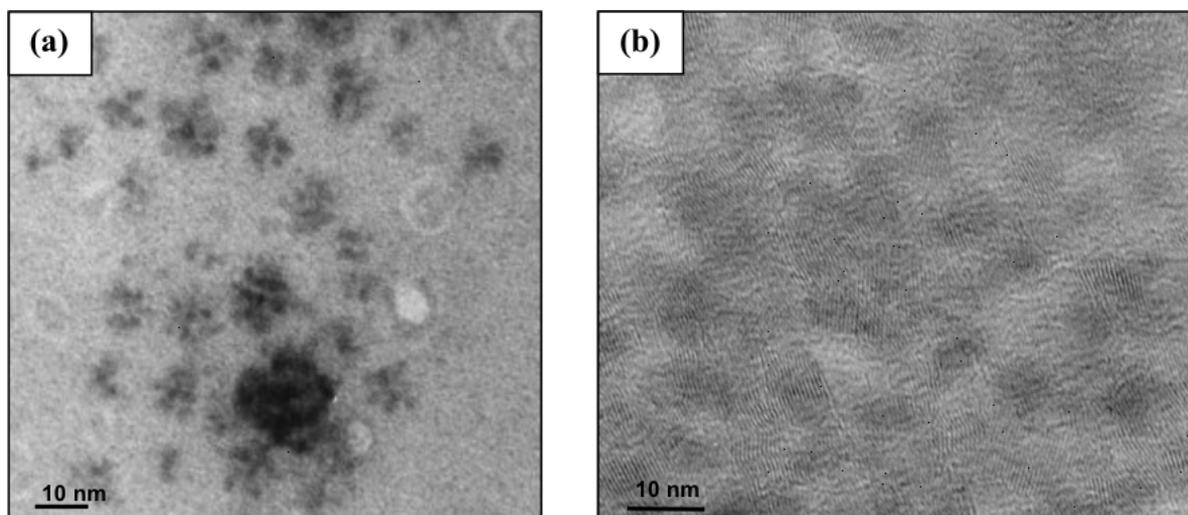


Figure 4 a, TEM image of Cu_2S nanoparticles; b, HRTEM image of Cu_2S nanoparticles.

Acknowledgements

We thank the Royal Society and the National Research Foundation (NRF) for support to Dr Neerish Revaprasadu and a programme of collaboration between UZULU and University of Manchester (UK).

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