Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2014) 38: 413 – 422

doi:10.3906/kim-1305-47

Deposition and characterization of Cu_9S_5 nanocrystals from unsymmetrical $[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3,5]_2Cu(II)$ and $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$ complexes by colloidal thermolysis method

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Received: 21.05.2013 • **Accepted:** 14.10.2013 • **Published Online:** 14.04.2014 • **Printed:** 12.05.2014

Abstract: Cu_9S_5 nanocrystals were synthesized from unsymmetrical $[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3,5]_2Cu(II)$ and $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2$ Cu(II) complexes by colloidal thermolysis in the presence of surfactant oleylamine. The unsymmetrical copper complexes were synthesized by the reaction of copper(II) acetate with *N*-[hexyl(methyl)carbamothioyl]-3,5-dinitrobenzamide and *N*-[ethyl(butyl)carbamothioyl]-4-nitrobenzamide. The complexes were used as single-source precursors for the preparation of Cu_9S_5 nanocrsytals. The Cu_9S_5 nanocrystals were characterized by X-ray powder diffraction and transmission electron microscopy.

Key words: Cu_9S_5 nanocrystals, p-XRD, crystallites, TEM, colloidal thermolysis, thiourea derivatives

1. Introduction

The emerging nanotechnology involves the development and utilization of nanostructures and devices with a size range from 1 nm (molecular size) to about 20 nm. Most of the inorganic materials reported for photovoltaic applications are either toxic or use less-abundant elements such as lead, cadmium, indium, or gallium. Relatively less toxic, abundant, and thus cheaper materials may be more promising even with overall lower efficiencies for photovoltaic applications.[1] Recent estimates of the annual electricity potential as well as material extraction costs and environmental friendliness led to the identification of inorganic or organic based materials that could be used in photovoltaic applications on a large scale. The most promising and efficient materials include iron and copper sulfide.[2,3] The properties and application of semiconducting nanostructured materials extensively depend on their crystal phase, size, composition, and shape as well as the processing technique for the production of highly tuned nanocrystals.[4]

Semiconducting nanostructured copper sulfides thin films and nanoparticles have been investigated for many uses including as p-type semiconductors in solar cells,[5–7] nanoscale switches,[8e] and cathodic materials for lithium rechargeable batteries.[9] Vaughan et al.[10] reported that in 1940 only the end member (Cu_2S) and CuS were known in the Cu–S system. By 1974 nine more copper sulfide phases had been identified,[11e] and in 2006 a total of 14 copper sulfide phases were recognized.[12] Some important known and promising forms of copper sulfide include chalcocite (Cu_2S), djurleite ($Cu_{31}S_{16}$ or $Cu_{1.94}S$), digenite (Cu_9S_5 or $Cu_{1.8}S$), anilite

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(Cu_7S_4 or $Cu_{1.75}S$), covellite (CuS), and villamaninite (CuS_2).[13] Semiconducting nanostructured thin films of copper sulfide have been prepared by various methods including RF-reactive sputtering,[14] spray pyrolysis,[15] successive ionic layer adsorption and reaction,[16] chemical bath deposition,[17e] and chemical vapor deposition.[18]

Acylthioureas containing different heterocyclic moieties and alkyl substituents are important ligands for the preparation of metal complexes and these precursors can be easily applied for the deposition of metal sulfide nanoparticles using different capping agents. Arslan and co-workers[19,20] reported the complexation of copper(II) and zinc(II) with acylthiourea ligands and concluded that the coordination was through multifunction S,O-donor atoms, using infrared spectroscopy and X-ray diffractions studies. Binzet and co-workers[21] reported that the complexes of methylthiourea have coordination through sulfur donor atoms.

We have previously reported biologically active acylthiourea derivatives containing benzothiazole, thiazole, and pyrimidine moieties and their metal complexes.[22−24] As part of our long-standing interest in the coordination chemistry of acylthioureas bearing different heterocyclic moieties, we here explore the preparation of copper sulfide nanocrystals from single-source precursors *bis*[*N*-[hexyl(methyl)carbamothioyl]-3,5-dinitrobenzamide]copper(II) and *bis*[*N*-[ethyl(butyl)carbamothioyl]-4-nitrobenzamide]copper(II). These unsymmetrical single-source precursors can be easily prepared in high yield from comparatively inexpensive and only mildly hazardous starting materials, making them ideal for the potential large-scale production of copper sulfide semiconducting nanostructured thin films and nanocrystals.

2. Experimental

2.1. Materials and physical measurements

4-Nitrobenzoyl chloride (≥98.0%), *N*-hexylmethylamine (99%), *N*-butylethylamine (99%), sodium thiocyanate (99%), copper(II) nitrate trihydrate (99.5%), tetrabutylammonium bromide (TBAB) (≥98%), oleylamine-approx. C18 content 80%–90%, and 3,5-dinitrobenzoyl chloride (≥98.0%) were purchased from Sigma-Aldrich. Elemental analysis of the ligands was performed using a PerkinElmer CHNS/O 2400. Infrared spectra were recorded on a Specac single reflectance attenuated total reflectance (ATR) instrument (4000–400 cm^{-1}, resolution 4 cm^{-1}). Atmospheric pressure chemical ionization mass spectrometry (MS-APCI) of the copper complexes was recorded on a Micromass Platform II instrument. Metal analysis of the complexes was carried out by Thermo iCap 6300 inductively coupled plasma optical emission spectroscopy (ICP-OES). Melting points were recorded on a Barloworld SMP10 melting point apparatus. Thermal stability of the copper complexes was studied by thermogravimetery in an inert atmosphere, at sample heating rate of 10 °C/min, with a DuPont 2000 ATG. X-ray powder diffraction (p-XRD) studies were performed on an Xpert diffractometer using Cu-Kα radiation. The samples were mounted flat and scanned between 20° and 65° with a step size of 0.05 with various count rates. The diffraction patterns were then compared to the documented patterns in the International Center Diffraction Data[e] (ICDD) index. Transmission electron microscopy (TEM) samples were prepared by evaporating a drop of a dilute suspension of the sample in n-hexane on a carbon-coated copper grid. The excess solvent was allowed to dry completely at room temperature. TEM images were collected on a Philips CM200 transmission electron microscope using an accelerating voltage of 200 kV.

2.2. Synthesis of the copper complexes

***Bis*[*N*-[hexyl(methyl)carbamothioyl]-3,5-dinitrobenzamide]copper(II) [(Hex)(Me)NC(S)NC(O)$C_6H_3(NO_2)_2$-3,5]$_2$Cu(II)**

To a 250-mL double-necked round-bottomed flask containing 3,5-dinitrobenzoyl chloride (0.01 mol) dissolved in anhydrous acetone (75 mL) and 0.3 mole% of tetrabutylammonium bromide (TBAB) in acetone was added dropwise a suspension of sodium thiocyanate in acetone (45 mL) and the reaction mixture was refluxed for 45 min. After cooling to room temperature, a solution of *N*-hexylmethylamine (0.01 mol) in acetone (25 mL) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into 5 times its volume of cold water, whereupon the acylthiourea precipitated. The solid product of acylthiourea was washed with water and purified by recrystallization from ethyl acetate. Light yellow in semisolid state. Mp: 98–99 °C. Yield: 3.3 g (78%). IR (ν_{max}, cm^{-1}): 3176 (NH), 2959, 2877 (C–H), 1685 (C=O), 1262 (C=S). ^{1}H NMR (400 MHz, $CDCl_3$) in δ (ppm) and J (Hz): δ 9.11 (t, 1H, J= 1.8), 8.83 (d, 2H, J = 1.8), 8.38 (bs, 1H, CON$\underline{H}$), 3.90 (t, 2H, N–C$\underline{H}_2$), 3.01(s, 3H, C$\underline{H}_3$), 2.57(m, 2H, –C$\underline{H}_2$–), 1.83 (m, 2H, –C$\underline{H}_2$–), 1.66 (m, 2H, –C$\underline{H}_2$–), 1.27 (m, 2H, –C$\underline{H}_2$–), 0.90 (t, 3H, C$\underline{H}_3$). Anal. calcd. for $C_{15}H_{20}N_4O_5S$: C, 48.90; H, 5.47; N, 15.21; S, 8.70. Found: C, 48.87; H, 5.49; N, 15.20; S, 8.70.

In the second step, a solution of copper nitrate (0.005 mol) in methanol (25 mL) was added dropwise to a solution of the acylthiourea ligand in a 1:2 ratio with a small excess of acylthiourea in ethanol (25 mL) at room temperature, and the resulting mixture was stirred for 3 h. The reaction mixture was filtered, washed with ethanol, and recrystallized from a THF:acetonitrile mixture (1:1, $v:v$). Green. Yield: 3.9 g (81%). IR (ν_{max}, cm^{-1}): 2926, 2856 (Ar–H), 1508 (C–O), 1537 (C–N), 1121 (C–S); Anal. calcd. for$_e$ $C_{30}H_{38}N_8O_{10}S_2$Cu: C, 45.13; H, 4.80; N, 14.04; S, 8.05; Cu, 7.96. Found: C, 44.78; H, 4.87; N, 14.00; S, 8.06; Cu, 7.72. Mass (MS-APCI) (m/z): 798 [M+, $C_{30}H_{38}N_8O_{10}S_2$Cu].

***Bis*[*N*-[ethyl(butyl)carbamothioyl]-4-nitrobenzamide]copper(II) [(Et)(Bu)NC(S)NC(O)C_6H_4-4-NO_2]$_2$Cu(II)**

To a 250-mL double-necked round-bottomed flask containing 4-nitrobenzoyl chloride (0.01 mol) dissolved in anhydrous acetone (75 mL) and 0.3 mole% of tetrabutylammonium bromide (TBAB) in acetone was added dropwise a suspension of sodium thiocyanate in acetone (45 mL) and the reaction mixture was refluxed for 45 min. After cooling to room temperature, a solution of *N*-butylethylamine (0.01 mol) in acetone (20 mL) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into 5 times its volume of cold water, whereupon the acylthiourea precipitated. The generated solid product of acylthiourea was washed with water and purified by recrystallization from the ethanol. Yellow. Mp: 89–90 °C. Yield: 3.3 g (90%). IR (ν_{max}, cm^{-1}): 3233 (NH), 2931, 2852 (C–H), 1691 (C=O), 1256 (C=S). ^{1}H NMR (400 MHz, $CDCl_3$) in δ (ppm): 8.45 (s, 1H, CONH), 8.12 (d, 2H$_{meta}$, p-nitrophenyl), 7.35 (d, 2H$_{ortho}$, p-nitrophenyl), 3.82 (t, 2H, CH_2), 3.54 (m, 2H, CH_2), 1.85 (m, 2H, CH_2),1.65 (m, 2H, CH_2), 0.98 (t, 3H, CH_3), 0.91 (t, 3H, CH_3); Anal. calcd. for $C_{14}H_{19}N_3O_3S$: C, 54.35; H, 6.19; N, 13.58; S, 10.36. Found: C, 54.32; H, 6.35; N, 13.57; S, 10.37. In the second step, a solution of copper nitrate (0.005 mol) in methanol (25 mL) was added dropwise to a solution of the acylthiourea ligand in a 1:2 ratio with a small excess of acylthiourea in ethanol (25 mL) at room temperature, and the resulting mixture was stirred for 3 h. The reaction mixture was filtered, washed with ethanol, and recrystallized from a THF:acetonitrile mixture (1:1, $v:v$). Dark brown. Mp: 175–176 °C. Yield: 3.3 g (78%). IR (ν_{max}, cm^{-1}): 2928, 2855 (Ar–H), 1508 (C–O), 1535 (C–N), 1140 (C–S); Anal. calcd.

for$_e$ $C_{28}H_{36}N_6O_6S_2Cu$: C, 49.43; H, 5.33; N, 12.35; S, 9.43; Cu, 9.34. Found: C, 49.51; H, 5.56; N, 12.22; S, 9.45; Cu, 9.05. Mass (MS-APCI) (m/z): 680 [M+, $C_{28}H_{36}N_6O_6S_2Cu$].

2.3. Synthesis of copper sulfide nanocrystals

Copper sulfide nanocrystals were prepared by pyrolyzing the copper complexes as precursors in oleylamine by colloidal thermolysis. In a typical reaction, 15 mL of oleylamine was refluxed under vacuum at 90 °C for 45 min, and then it was purged with nitrogen gas for 30 min at the same temperature. Then about 0.25 g of precursor was added to hot oleylamine and the reaction temperature was slowly increased to a desired point (170 and 230 °C) and the temperature was maintained for 1 h and the mixture was allowed to cool to room temperature. The black precipitate generated during the process was separated by centrifugation at 25,000 rpm.

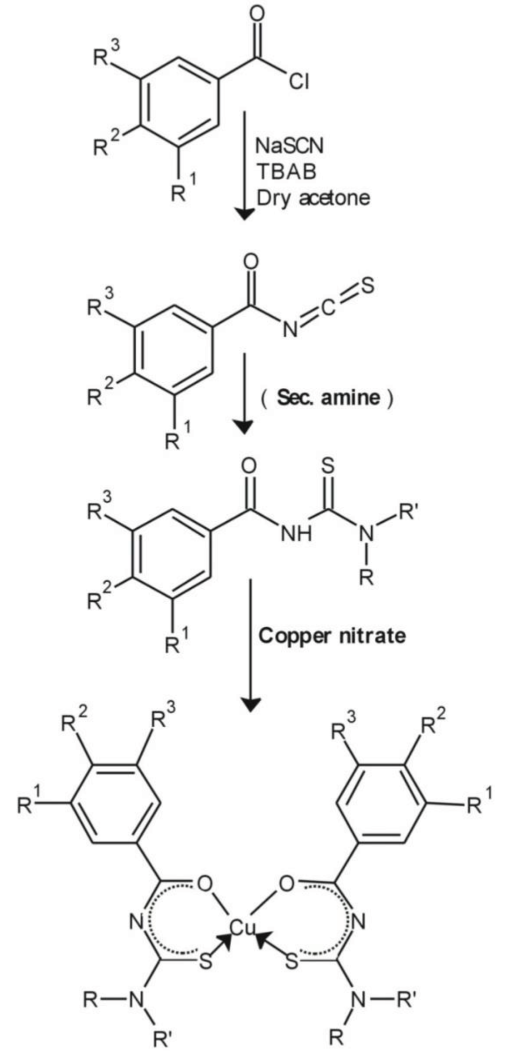
3. Results and discussion

The synthetic pathway for unsymmetrical acylthiourea derivatives and their copper complexes described in this communication is outlined in the Scheme. The acylthiourea ligands and copper complexes were synthesized according to the reported procedures[25−33] with minor modifications. The use of phase transfer catalyst is a well known method and is extensively applied in heterogeneous reaction systems.[34,35e] To improve the yield of aroylthiourea ligands, we used TBAB as phase transfer catalyst in our designed reactions. The reaction proceeds via nucleophilic addition of the secondary amine to the acylisothiocyanate. IR spectra of acylthiourea ligands and the copper complexes in the region 4000–400 cm^{-1} were compared and assigned on careful comparison. N,N'-disubstituted thioureas behave both as monodentate and bidentate ligands, depending upon the reaction conditions.[36] The characteristic bands of N,N'-disubstituted thioureas are 3233–3276 (NH), 2852–2959 Ph (CH), 1691–1685 (C=O), and 1262–1256 (C=S), and there is a slight shift of (C=O) and (C=S) groups' stretching frequencies due to coordination of the ligands to the copper atom.

As is well known, acythioureas usually act as bidentate ligands to transition-metal ions through the acyl oxygen and sulfur atoms.[37−40] The IR spectra of the copper(II) complexes show significant changes when compared with the IR spectra of the corresponding acylthiourea ligands. The IR spectra of the complexes show absorption bands at υ_{max}: 2855–2926 Ph (CH), 1508 (C–O), 1537–1535 (C–N), and 1140–1121 (C–S) cm^{-1}. The most prominent changes are the N–H stretching frequency at ∼3200 cm^{-1} in the free acylthiourea ligands, which disappears completely, in full agreement with both ligands and copper complexes and the complexation reaction. The spectroscopic data clearly indicate the loss of the proton originally bonded to the nitrogen atom of the (NH–CO) amide groups. Another prominent change is observed for the carbonyl functional group stretching vibrations. The stretching frequencies due to the carbonyl functional groups (1691 and 1685 cm^{-1}) in the free acylthiourea ligands are shifted towards lower frequencies upon complexation, indicating that ligands are coordinated to copper(II) ion through the O,S-donor atoms.[41−45] IR spectroscopic data of the complexes with the values of the free acylthiourea ligands indicate that the coordination of acylthiourea ligands to the copper atom has a significant effect on υ(N-H), υ(C=O), and υ(C=S) frequencies.

3.1. Thermal decomposition studies of copper(II) complexes

The TGA pattern of the complex $[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3,5]_2Cu(II)$ shows 2-step decomposition (Figure 1a). The first step starts at 164 °C and is accomplished at 335 °C with weight loss of 67.24%. The major part of the complex degraded sharply in the first region (164–335 °C). In the second step, the decom-



Copper complexes	R^1	R^2	R^3	R	R’
$[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3,5]_2Cu(II)$	NO_2	H	NO_2	Hexyl	Methyl
$[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$	H	NO_2	H	Butyl	Ethyl

Scheme

position starts at 343 °C and is accomplished at 586 °C. The decomposition ends at about 600 °C to leave a residue of 21.01% of the initial mass, which is slightly higher than the 17.34% calculated for complete conversion to copper sulfide material. The residual weight remains the same from 550 °C to higher temperatures, which indicates the expected stable phase of copper sulfide. TGA of the complex $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$ shows 2-step decomposition with rapid weight loss between 243 and 324 °C and the second step between 331 and 442 °C as shown in Figure 1b. The major part of the complex degraded sharply in the region of 270–300 °C. The decomposition ends at about 600 °C to leave a residue amount of 18.63%, which is very close to the accumulative mass of decomposed product copper sulfide (calcd. 18.77%). Arslan and co-workers reported the mechanism of thermal decomposition of some thioureas and their metal complexes.[46−50]

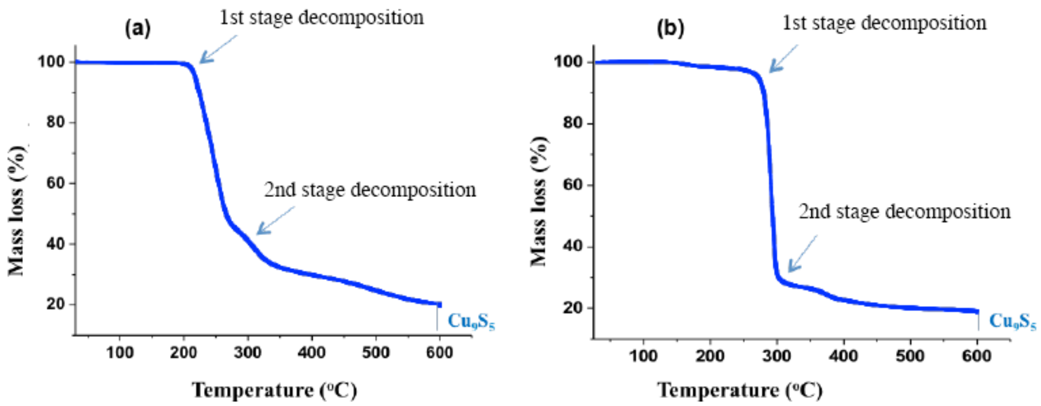


Figure 1. TGA of copper complex [(Hex)(Me)NC(S)NC(O)$C_6H_3(NO_2)_2$-3,5$]_2$Cu(II) (**a**) and [(Et)(Bu)NC(S) NC(O) C_6H_4-4-$NO_2]_2$Cu(II) (**b**).

3.2. X-ray diffraction and transmission electron microscopic characterization of digenite Cu_9S_5 nanocrystals deposited from [(Hex)(Me)NC(S)NC(O)$C_6H_3(NO_2)_2$-3,5$]_2$Cu(II)

The XRD pattern for the Cu_9S_5 nanocrystals synthesized from precursor [(Hex)(Me)NC(S)NC(O)$C_6H_3(NO_2)_2$-3,5$]_2$Cu(II) is shown in Figure 2. The synthesis of copper sulfide nanocrystals was carried out at 170 °C and 230 °C. No deposition was obtained below 170 °C (Figure 2a). At 230 °C (Figure 2b) the XRD pattern of Cu_9S_5 (digenite) nanocrystals shows diffractions of rhombohedral Cu_9S_5 and the space group R-3m (166) with major diffraction peaks of (0015), (107), (1010), (0114), (110), and (205) planes (ICDD: 026-0476) as shown in the Table. In the XRD pattern, an extra peak 'x' was also observed. This peak may be due to some impurity present but unfortunately its nature could not be identified. The TEM image (Figure 3) showed the deposited Cu_9S_{5e} crystallites are rectangular and irregular shaped. There was a certain degree of agglomeration and size of the particles could be approximated to 250–600 nm in length.

Table. Powder X-ray crystal data of the decomposed material from complexes.

Copper sulfide, Cu_9S_{5e} [ICDD:026-0476]			
Crystal system		Rhombohedral	
Space group		R-3m	
Cell volume		638.44 Å^3	
Z		3	
Cell parameters		a = 3.919 Å $\alpha = 90.00°$ b = 3.919 Å $\beta = 90.00°$ c = 48.000 Å $\gamma = 120.00°$	
No.	Pos. [2θ]	d-spacing d(Å)	hkl matched with Cu_9S_5
1	27.8572	3.2000	0015
2	29.3357	3.0420	107
3	30.2301	2.9540	018
4	32.2793	2.7710	1010
5	35.9058	2.4990	1013
6	41.5629	2.1710	0117
7	46.2976	1.9594	110
8	54.8994	1.6710	205

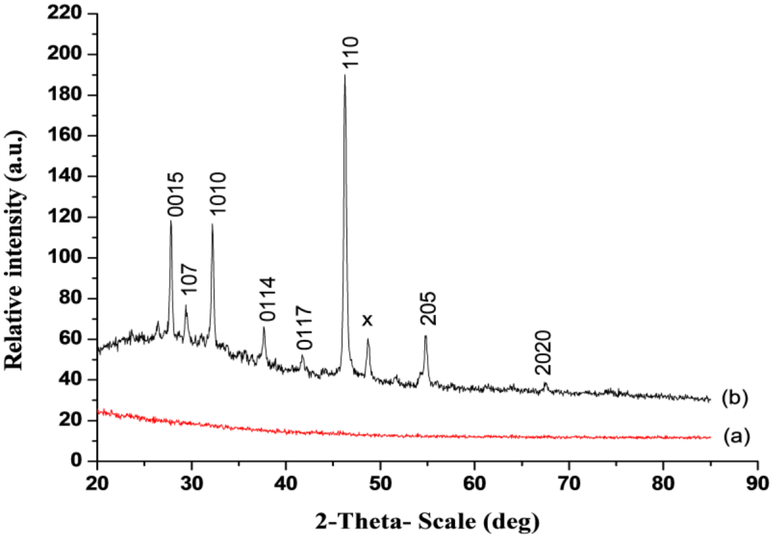


Figure 2. XRD pattern of Cu_9S_5 nanocrystals prepared at (a) 170 °C (b) 230 °C from $[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3,5]_2Cu(II)$.

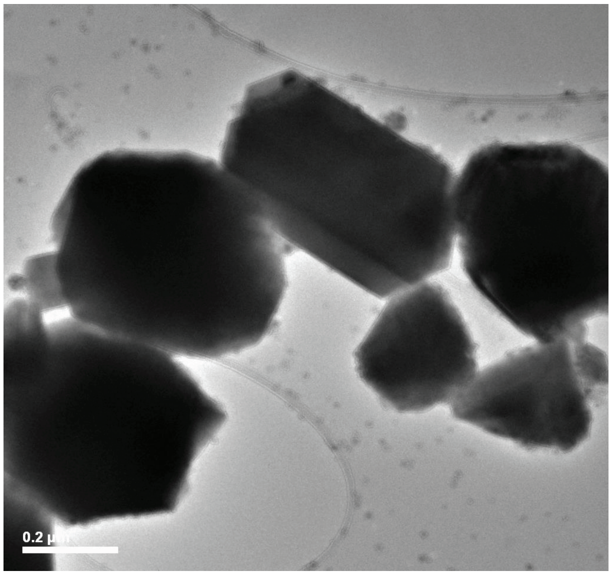


Figure 3. TEM image of Cu_9S_5 nanocrystals from $[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3,5]_2Cu(II)$.

3.3. X-ray diffraction and transmission electron microscopic characterization of digenite Cu_9S_5 nanocrystals deposited from $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$

The XRD pattern for the Cu_9S_5 nanocrystals synthesized from precursor $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$ is shown in Figure 4. The synthesis of copper sulfide nanocrystals was carried out at 170 °C and 230 °C. No deposition was obtained below 170 °C (Figure 4a). At 230 °C (Figure 4b) the XRD pattern of Cu_9S_5 (digenite) nanocrystals shows diffractions of rhombohedral Cu_9S_5 and the space group R-3m (166) with major diffraction peaks of (0015), (107), (1010), (110), and (205) planes (ICDD: 026-0476). The TEM image (Figure 5) showed that the deposited particles are in trigonal shaped and size of the particles could be approximated to 17–450 nm in length. Reaction time, temperature, concentration, and the selection of reagents and surfactants play an important role to control the size, shape, and quality of the particles. Generally the particle size increases with an increase in reaction time and temperature.[51]

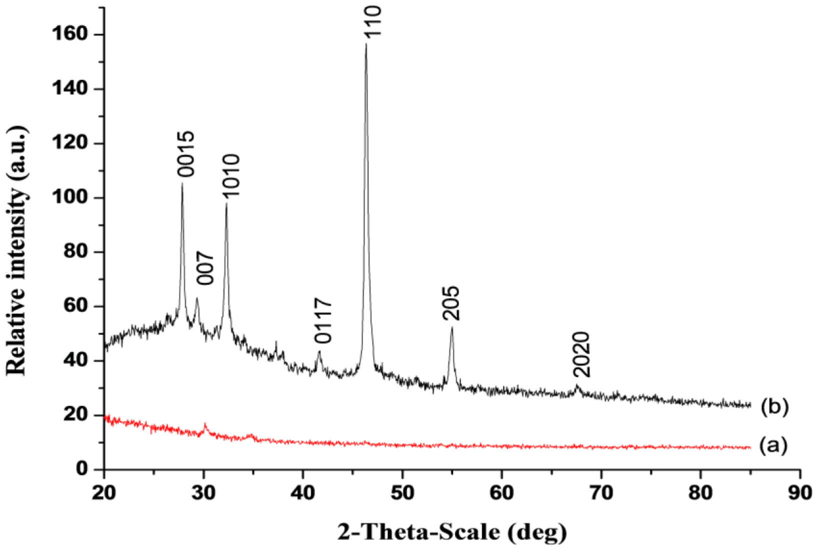


Figure 4. XRD pattern of Cu_9S_5 nanocrystals prepared at (a) 170 °C (b) 230 °C from $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$.

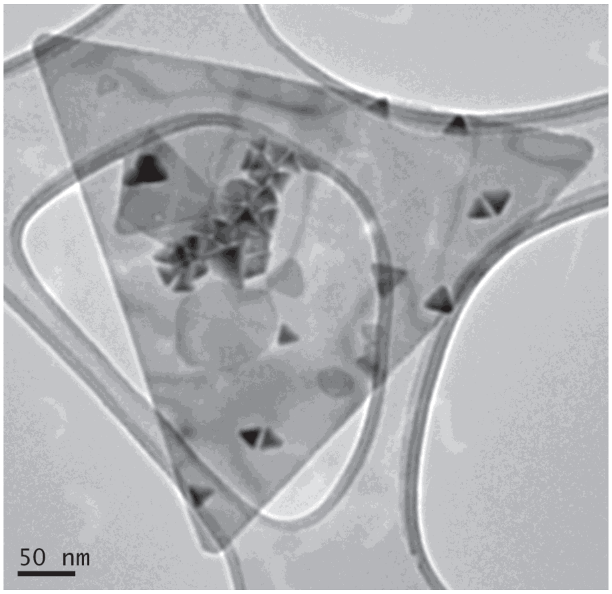


Figure 5. TEM image of Cu_9S_5 nanocrystals from $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$.

4. Conclusions

A new approach has been introduced to synthesize Cu_9S_5 nanocrystals from single source precursors $[(Hex)(Me)NC(S)NC(O)C_6H_3(NO_2)_2\text{-}3{,}5]_2Cu(II)$ and $[(Et)(Bu)NC(S)NC(O)C_6H_4\text{-}4\text{-}NO_2]_2Cu(II)$ by colloidal thermolysis. The prepared Cu_9S_5 nanocrystals are rectangular and trigonal shaped crystallites 250–600 nm and

17–450 nm in length, respectively. These newly synthesized copper complexes may also be useful as applicable precursors for the deposition of TOPO capped (tri-n-octylphosphineoxide) nanoparticles of copper sulfide.

Acknowledgment

Dr Sohail Saeed would like to acknowledge the Higher Education Commission (HEC), Government of Pakistan, for its financial support.

References

1. Monajjemi, M.; Baei, M. T.; Mollaamin, F. *Russian J. Inorg. Chem.* **2008**, *53*, 1430–1437.
2. Monajjemi, M.; Mahdavian, L.; Mollaamin, F.; Khaleghian, M. *Russian J. Inorg. Chem.* **2009**, *54*, 1465–1473.
3. Zare, K.; Daroule, M.; Mollaamin, F.; Monajjemi, M. *Int. J. Phys. Sci.* **2011**, *6*, 2536–2540.
4. Sun, Y. G.; Xia, Y. N. *Science* **2002**, *298*, 2176–2179.
5. Lee, H.; Yoon, S. W.; Kim, E. J.; Park, J. *Nano Lett.* **2007**, *7*, 778–784.
6. Wu, Y.; Wadia, C.; Ma, W.; Sadtler, B.; Alivisatos, A. P. *Nano Lett.* **2008**, *8*, 2551–2555.
7. Wadia, C.; Alivisatos, A. P.; Kammen, D. M. *Environ. Sci. Technol.* **2009**, *43*, 2072–2077.
8. Sakamoto, T.; Sunamura, H.; Kawaura, H. *Appl. Phys. Lett.* **2003**, *82*, 3032–3034.
9. Chung, J. S.; Sohn, H. J. *J. Power Sources* **2002**, *108*, 226–231.
10. Vaughan, D. J.; Craig, J. R. *Mineral Chemistry of Metal Sulfides*, ed. W. B. Harland, S. O. Agrell, A. H. Cook and N. F. Hughes, Cambridge University Press, Cambridge, UK, 1978, pp. 290–292.
11. Fleet, M. E. *Rev. Mineral. Geochem.* **2006**, *61*, 365–420.
12. Koch, D. F. A.; McIntyre, R. *J. Electroanal. Chem.* **1976**, *71*, 285–296.
13. He, Y. B.; Polity, A.; Osterreicher, I.; Pfisterer, D.; Gregor, R.; Meyer, B. K.; Hardt, M. *Phys. B*, **2001**, *308–310*, 1069–1073.
14. Wang, S. Y.; Wang, W.; Lu, Z. H. *Mater. Sci. Eng. B* **2003**, *103*, 184–188.
15. Sartale, S. D.; Lokhande, C. D. *Mater. Chem. Phys.* **2000**, *65*, 63–67.
16. Hu, H.; Nair, P. K. *Surf. Coat. Technol.* **1996**, *81*, 183–189.
17. Kemmler, K.; Lazell, M.; O'Brien, P.; Otway, D. J.; Park, J. H.; Walsh, J. R. *J. Mater. Sci.: Mater. Electron.* **2002,** *13*, 531–535.
18. Moloto, M. J.; Revaprasadu, N.; O'Brien, P.; Malik, M. A. *J. Mater. Sci. Mater. Electron.* **2004**, *15*, 313–316.
19. Arslan, H.; Flörke, U.; Kulcu, N.; Emen, M. F. *J. Coord. Chem.* **2006**, *59*, 223–228.
20. Binzet, G.; Arslan, H.; Flörke, U.; Kulcu, N.; Duran, N. *J. Coord. Chem.* **2006**, *59*, 1395–1406.
21. Bailey, R. A.; Peterson, T. R. *Can. J. Chem.* **1967**, *45*, 1135–1142.
22. Saeed, S.; Rashid, N.; Jones, P. G.; Ali, M.; Hussain, R. *Eur. J. Med. Chem.* **2010**, *45*, 1323–1331.
23. Saeed, S.; Rashid, N.; Jones, P. G.; Hussain, R.; Bhatti, M. H. *Cent. Eur. J. Chem.* **2010**, *8*, 550–558.
24. Saeed, S.; Rashid, N.; Jones, P. G.; Tahir, A. *J. Heterocyclic. Chem.* **2011**, *48*, 74–82.
25. Saeed, S.; Rashid, N.; Hussain, R.; Jones, P. G. *Eur. J. Chem.* **2011**, *2*, 77–82.
26. Saeed, S.; Wong, W.-T. *J. Heterocyclic. Chem.* **2012**, *49*, 580–584.
27. Saeed, S.; Rashid, N.; Bhatti, M. H.; Jones, P. G. *Turk. J. Chem.* **2010**, *34*, 761–770.
28. Saeed, S.; Rashid, N.; Ali, M.; Hussain, R.; Jones, P. G. *Eur. J. Chem.* **2010**, *1*, 221–227.
29. Saeed, S.; Rashid, N.; Ali, M.; Hussain, R. *Eur. J. Chem.* **2010**, *1*, 200–205.

30. Saeed, S.; Rashid, N.; Hussain, R.; Jasinski, J. P.; Keeley, A. C.; Khan, S. *J. Coord. Chem.* **2013**, *66*, 126–138.
31. Saeed, S.; Hussain, R.; Ali, M. *J. Heterocyclic. Chem.* **2013**, *50*, 237–243.
32. Saeed, S.; Rashid, N.; Malik, M. A.; O'Brien, P.; Wong, W.-T. *New J. Chem.* **2013**, *37*, 3214–3221.
33. Saeed, S.; Rashid, N.; Ahmad, K. S. *Turk. J. Chem.* **2013**, *37*, 796–804.
34. Ke, S.-Y.; Xue, S.-J. *ARKIVOC* **2006**, x, 63–68.
35. Wei, T. B.; Chen, J. C.; Wang, X. C. *Synth. Commun.* **1996**, *26*, 1147–1152.
36. Fregona, D.; Giovagnini, L.; Ronconi, L.; Marzano, C.; Trevisan, A.; Sitran, S.; Biondi, B.; Bordin, F. *J. Inorg. Biochem.* **2003**, *93*, 181–189.
37. El-Reash, G. M. A.; Taha, F. I.; Badr, G. *Transition Met. Chem.* **1990**, *15*, 116–119.
38. Che, D. J.; Yao, X. L.; Li, G.; Li, Y. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1853.
39. Richter, R.; Beyer, L.; Kaiser, J. *Z. Anorg. Allg. Chem.* **1980**, *461*, 67–73.
40. Beyer, L.; Hoyer, E.; Liebscher, J.; Hartmann, H. *Z. Chem.* **1980**, *21*, 81–84.
41. Irving, A.; Koch, K. R; Matoetoe, M. *Inorg. Chim. Acta.* **1993**, *206*, 193–198.
42. Koch, K. R.; Sacht, C.; Bourne, S. *Inorg. Chim. Acta* **1995**, *232*, 109–115.
43. Mikami, M.; Nakagawa, I.; Shimanouch, T. *Spectrochim. Acta* **1967**, *23A*, 1037–1042.
44. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed, Wiley, New York, NY, USA, 1986.
45. Arslan, H.; Külcü, N.; Flörke, U. *Trans. Metal. Chem.* **2003**, *28*, 816–819.
46. Özpozan, N.; Özpozan, T.; Arslan, H.; Karipcin, F.; Külcü, N. *Thermochimica Acta* **1999**, *336*, 97–103.
47. Özpozan, N.; Arslan, H.; Özpozan, T.; Merdivan, M.; Külcü, N. *J. Therm. Anal. Calorim.* **2000**, *61*, 955–965.
48. Özpozan, N.; Arslan, H.; Özpozan, T.; Özdes, N.; Külcü, N. *Thermochimica Acta* **2000**, *343*, 127–133.
49. Arslan, H. *J. Therm. Anal. Calorim.* **2001**, *66*, 399–407.
50. Avşar, G.; Külcü, N.; Arslan, H. *Turk. J. Chem.* **2002**, *26*, 607–615.
51. Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183–184.