

Aerosol-assisted chemical vapor deposition of copper sulfide nanostructured thin film from newly synthesized single-source precursor

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Abstract: The copper(II) complex of *N*-[ethyl(butyl)carbamoithiyl]-3,5-dinitrobenzamide (**1**) has been synthesized and characterized by elemental analysis, IR spectroscopy, and atmospheric pressure chemical ionization-mass spectrometry. Thermogravimetric analysis shows that complex **2** decomposes in 2 steps to form copper sulfide. The complex was used as a single-source precursor for the deposition of copper sulfide thin film by aerosol-assisted chemical vapor deposition at 350 °C. The powder X-ray diffraction pattern of thin film of the complex showed the deposition of monoclinic roxbyite Cu_7S_4 and orthorhombic anilite Cu_7S_4 phases at 350 °C with spherical crystallites. The degree of film surface roughness was determined by atomic force microscopy. The scanning electron microscopy and energy dispersive X-ray analysis results showed the uniform distribution of copper sulfide in the film, which makes it a useful semiconducting material on a structured surface.

Key words: Copper complex, thin film, aerosol-assisted chemical vapor deposition, scanning electron microscopy, powder X-ray diffraction

1. Introduction

Recently, nanostructured materials have attracted great attention in the fields of experimental and theoretical chemistry sciences^{1–3} Due to the extensive dependence of the properties and application of nanostructured semiconductors on their crystal phase, size, composition and shape, the synthesizing of highly tuned nanocrystals has been a challenging issue⁴

Copper sulfide thin films and nanoparticles have been investigated for many uses, including uses as p-type semiconductors in solar cells,^{5–7} nanoscale switches,⁸ and cathodic materials for lithium rechargeable batteries.⁹ Vaughan and Craig¹⁰ reported that in 1940 only the end member (Cu_2S) and CuS were known in the Cu-S system. By 1974, 9 more copper sulfide phases had been identified,^{11,12} and in 2006 a total of 14 copper sulfide phases were recognized.¹² Some known forms of copper sulfide include chalcocite (Cu_2S), djurleite ($\text{Cu}_{31}\text{S}_{16}$ or $\text{Cu}_{1.94}\text{S}$), digenite (Cu_9S_5 or $\text{Cu}_{1.8}\text{S}$), anilite (Cu_7S_4 or $\text{Cu}_{1.75}\text{S}$), covellite (CuS), and villamaninite (CuS_2).^{7–13} 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,¹⁷ and chemical vapor deposition.¹⁸

Thiourea and its alkyl derivatives are important precursors for the preparation of metal sulfide nanoparticles. Besides focusing on the applications of these ligands, special attention has been placed on their coordination

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chemistry to different metal atoms because of the various potential donor sites that these ligands possess.¹⁹ Arslan et al.²⁰ and Benzet et al.²¹ reported the complexation of Cu(II) and Zn(II) with thiourea derivatives and concluded that the coordination was through the sulfur and oxygen atom, using infrared spectroscopy and X-ray diffractions to determine the coordination. In addition, complexes prepared using the alkyl thiourea, such as methylthiourea, showed, using infrared spectroscopy, that the coordination also was through sulfur.²¹ Thiourea and its derivatives were used as a source of sulfur because their advantages in this regard are that they are stable for a long time, easy to synthesize, inexpensive, and able to yield good-quality crystalline semiconductor particles.

Our interest in such precursors led us to synthesize an unsymmetrical copper complex to be used as a single-source precursor for copper sulfide. The single-source precursor can be easily synthesized in high yield from relatively inexpensive and only mildly hazardous starting materials, making it ideal for the potential large-scale manufacturing of copper sulfide nanostructured thin film.

2. Experimental section

2.1. Materials and reagents

Analytical grade *N*-ethylbutyl amine (98%), sodium thiocyanate (99%), copper(II) nitrate trihydrate (99.5%), tetrabutylammonium bromide (TBAB) ($\geq 98\%$) and 3,5-dinitrobenzoyl chloride ($\geq 98.0\%$) were purchased from Sigma-Aldrich. Analytical grade solvents such as tetrahydrofuran (THF), toluene, acetonitrile, *n*-hexane, dichloromethane, ethanol, methanol, chloroform, ethyl acetate and others were purchased from Sigma-Aldrich and Riedal de Haën and ethanol and acetone were dried using standard procedures²² All the synthetic manipulations were carried out in air except for the thermolysis experimentations. The colloidal thermolysis experiments were carried out under N₂ inert atmosphere. The demonstration of aerosol-assisted chemical vapor deposition (AACVD) was carried out under argon inert atmosphere.

2.2. Physical measurements

Elemental analysis was carried out using a PerkinElmer CHNS/O 2400. Obtained results were within 0.4% of the theoretical values. Infrared spectra were recorded on a Specac single-reflectance Attenuated Total Reflectance instrument (4000–400 cm⁻¹, resolution 4 cm⁻¹). Atmospheric pressure chemical ionization mass spectrometry (MS-APCI) of the copper complex was recorded on a Micromass Platform II instrument. Metal analysis of the complex 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 complex was studied by thermogravimetry in an inert atmosphere, at a 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-K α radiation. The sample was mounted flat and scanned between 20° and 65° with a step size of 0.05 with various count rates. The diffraction pattern was then compared to the documented patterns in the International Centre for Diffraction Data (ICDD) index.

2.3. Preparation of the ligand and copper(II) complex

2.3.1. Synthesis of *N*-[ethyl(butyl)carbamothioyl]-3,5-dinitrobenzamide (1)

A solution of 3,5-dinitrobenzoyl chloride (0.01 mol) in anhydrous acetone (80 mL) and 3% TBAB in acetone was added drop-wise to a suspension of sodium thiocyanate in acetone (50 mL) and the reaction mixture was

refluxed for 45 min. After cooling to room temperature, a solution of *N*-butylethyl amine (0.01 mol) in acetone (25 mL) was added and the resulting mixture was refluxed for 2 h. The reaction mixture was poured into 5 times its volume of cold water, whereupon the thiourea precipitated. The solid product was washed with water and purified by recrystallization from an ethanol–dichloromethane mixture (1:2). Light yellow, mp 126–127 °C. Yield: 3.0 g (74%). IR (ν_{max}/cm^{-1}): 3235 (NH), 2922, 2845 (C-H), 1691 (C=O), 1258 (C=S). ^1H NMR (400 MHz, CDCl_3) in δ (ppm) and J (Hz): δ 9.10 (t, 1H, $J = 1.8$), 8.84 (d, 2H, $J = 1.8$), 8.35 (bs, 1H, CONH), 3.91 (t, 2H, N-CH₂), 3.55 (m, 2H, N-CH₂), 1.83 (m, 2H, -CH₂-), 1.44 (m, 2H, -CH₂-), 1.20 (t, 3H, CH₃), 0.93 (t, 3H, CH₃). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_5\text{S}$: C, 47.45; H, 5.12; N, 15.81; S, 9.05. Found: C, 47.47; H, 5.09; N, 15.82; S, 9.03.

2.3.2. Synthesis of *Bis*[*N*-[ethyl(butyl)carbamothioyl]-3,5-dinitrobenzamide]copper(II) (2)

To a stirred solution thiourea ligand (3.54 g, 0.01 mol) in ethanol (30 mL) was added drop-wise a solution of copper nitrate (1.20 g, 0.005 mol) in ethanol (30 mL). The reaction mixture was stirred for 3 h. The reaction mixture was filtered, washed with ethanol, and recrystallized from THF/acetonitrile mixture (1:1). Dark brown. Yield: 3.6 g (77%). IR (ν_{max}/cm^{-1}): 2928, 2855 (Ar-H), 1507 (C-O), 1536 (C-N), 1153 (C-S). Anal. Calcd. for $\text{C}_{28}\text{H}_{34}\text{N}_8\text{O}_{10}\text{S}_2\text{Cu}$: C, 43.66; H, 4.45; N, 14.55; S, 8.33; Cu, 8.25. Found: C, 43.11; H, 4.02; N, 14.95; S, 8.32; Cu, 7.94. Mass (MS-APCI) (major fragment, m/z): 770 [M^+ , $\text{C}_{28}\text{H}_{34}\text{N}_8\text{O}_{10}\text{S}_2\text{Cu}$].

2.4. Deposition of copper sulfide thin film by AA-CVD

Experiments were designed according to those reported by us previously. In a typical experiment, 0.25 g of the precursor was dissolved in 15 mL of THF and the mixture was loaded in a 2-necked, 100-mL round-bottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This round-bottom flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven soda glass substrates (approx. 1×2 cm) were placed inside the reactor tube, which was placed in a Carbolite furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor vapor reached the heated substrate surface where thermally induced reactions and film deposition took place.

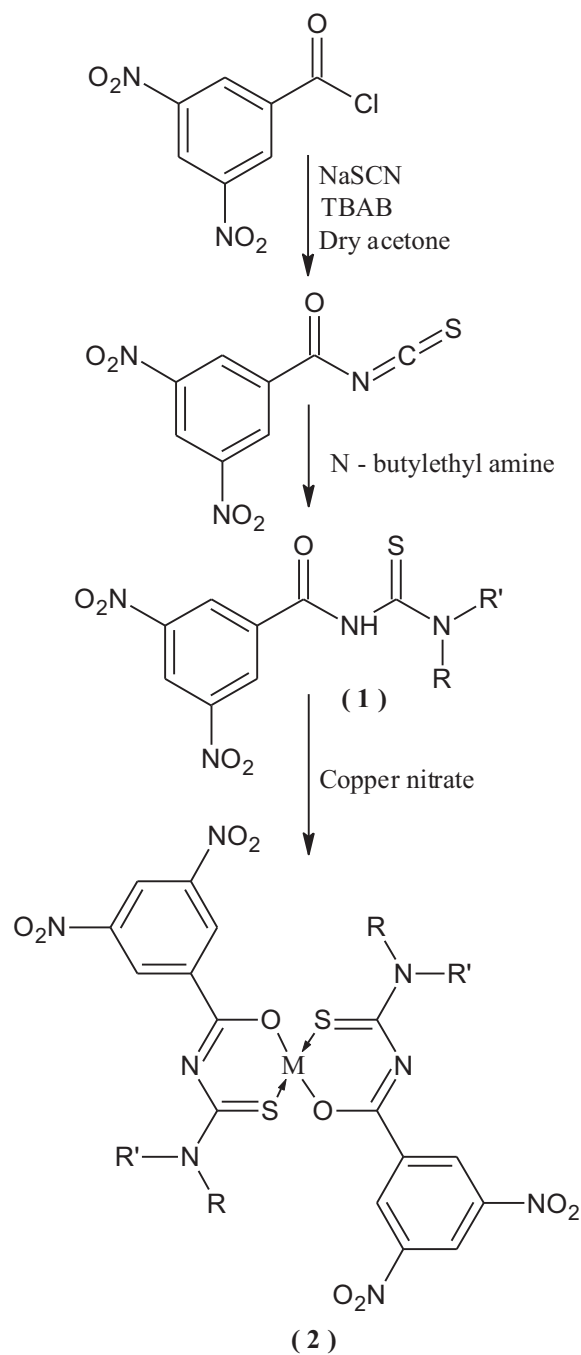
3. Results and discussion

Most of the materials reported for photovoltaic use are either toxic or use less-abundant elements such as lead, cadmium, indium, or gallium. Less-toxic, abundant, and thus cheaper materials may be more promising even with overall lower efficiencies. Recent estimates of the annual electricity potential as well as material extraction costs and environmental friendliness led to the identification of materials that could be used in photovoltaic applications on a large scale.²³ The most promising materials include iron and copper sulfide.

3.1. Preparation and spectroscopic characterization

The bidentate ligand was synthesized from 3,5-dinitrobenzoyl chloride, sodium thiocyanate, and *N*-butylethyl amine in anhydrous acetone. The thiourea derivative (1) and its copper complex (2) were synthesized according to the reported procedure^{24–29} with minor modifications as presented in the Synthesis Scheme. The use of

phase-transfer catalyst as a method of agitating a heterogeneous reaction system is gaining recognition.^{30,31} In search of improved methods to prepare the target thiourea by reacting isothiocyanates with nucleophiles, we have found that the use of TBAB as phase-transfer catalyst can produce isothiocyanates in good yield. The reaction proceeds via a nucleophilic addition of the secondary amine to the isothiocyanate. We have conducted our reaction using TBAB as phase transfer catalyst to synthesize the thiourea derivative.



Scheme. Preparation of thiourea derivative (1) and its copper complex (2).

A four-coordinated copper(II) complex (**2**) was synthesized by reacting copper nitrate with *N*-[ethyl(butyl) carbamothioyl]-3,5-dinitrobenzamide (**1**) in ethanol. The copper(II) complex (**2**) obtained is green in color, air-stable, nonhygroscopic in nature, and soluble in THF, acetonitrile, dichloromethane, chloroform, DMSO, and DMF. The solid-state IR spectra of the thiourea derivative ligand and the metal complex in the region of 4000–400 cm^{-1} were carefully compared and assigned. Thiourea ligands behave both as a monodentate and bidentate ligands, depending upon the reaction conditions. The characteristic bands of thiourea ligand are between or near to 3235 (NH), 2922, 2845 Ph(CH), 1691 (C=O), and 1258 (C=S), and there is a slight shift of (CN) and (CS) groups' stretching frequencies due to coordination of the ligand to the copper atom. As is well known, acylthioureas usually act as bidentate ligands to transition-metal ions through the acyl oxygen and sulfur atoms.^{32–34} The FT-IR spectrum of the complex showed significant changes when compared with the FT-IR spectrum of the corresponding ligand. The IR spectrum of the complex showed absorption bands at ν_{max}/cm^{-1} : 2928, 2855 (Ar-H), 1507 (C-O), and 1153 (C-S). The most striking change was that the N-H stretching frequency at 3235 cm^{-1} in the free ligand disappeared completely, in agreement with both ligand and complex structure and the complexation reaction. This indicates the loss of the proton originally bonded to the nitrogen atom of the (NH-CO) amide group. Another striking change was observed for the carbonyl stretching vibration. The vibrational frequency due to the carbonyl (1691 cm^{-1}) group in the free ligand was shifted towards lower frequency upon complexation, confirming that the ligand is coordinated to the copper(II) ion through the oxygen and sulfur donor atoms.^{35–39} A comparative absorption pattern of the complex with the values of the free ligand demonstrate that the coordination of the thiourea ligand to the copper atom has a significant effect on $\nu(\text{NH})$, $\nu(\text{CO})$, and $\nu(\text{CS})$ frequencies.

3.2. The AA-CVD deposition of copper sulfide thin film from *Bis*[*N*-[ethyl(butyl) carbamothioyl]-3,5-dinitrobenzamide]copper(II) (**2**)

3.2.1. Thermogravimetric analysis of copper(II) complex (**2**)

The thermogram of complex **2** shows 2 stages of weight loss (Figure 1). The first step begins at 38 °C and is accomplished at 225 °C. The second starts at 225 °C and is completed at 583 °C, with residue at 600 °C

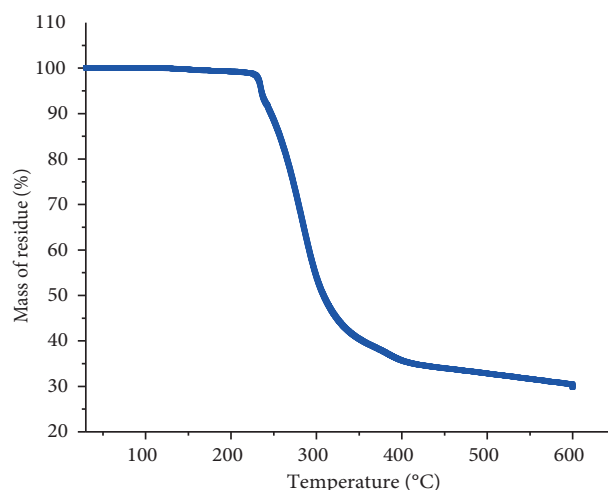


Figure 1. Thermogravimetric plot showing loss in weight with increase in temperature for complex (**2**).

amounting to 29.82% of the initial weight. The residual weight (29.82%) is higher, but considerably close to the expected composition for CuS (calc. 16.58%), the presence of which was further supported by the XRD analysis of the residue.

3.2.2. X-ray diffraction studies of deposited nanostructured thin film

Using the above TGA data, the AA-CVD experiment was run at 350 °C. At 350 °C the XRD pattern from this film shows 2 types of phases (Figure 2). The diffraction pattern of the dominant phase is monoclinic roxbyite (Cu_7S_4) in the space group C2/m (12) with major diffraction peaks of (1600), (804), (2001), and (0160) planes (ICDD: 023-0958). The second phase is orthorhombic anilite (Cu_7S_4) in space group Pnma (62) with major diffraction peaks of (202), (220), and (224) planes (ICDD: 022-0250); cell parameters are listed in the Table.

Table. Powder X-ray crystal data of the decomposed material from copper complex (2).

Copper sulfide, Cu_7S_4 [ICDD: 033-0489]			
Crystal system		Orthorhombic	
Space group		Pnma	
Cell volume		685.14 Å ³	
Z		4	
Cell parameters		b = 11.078 Å β = 90.00° a = 7.906 Å α = 90.00° c = 7.822 Å γ = 90.00°	
No.	Pos. [2 θ]	d-spacing d(Å)	hkl matched with Cu_7S_4
1	27.6983	3.2180	202
2	29.0043	3.0760	113
3	32.1719	2.7800	220
4	37.7673	2.3800	302
5	42.0905	2.1450	321
6	44.0053	2.0560	133
7	46.2327	1.9620	224
8	54.9421	1.6698	026
9	67.3055	1.3900	440

3.2.3. Scanning electron and atomic force microscopic studies of the nanostructured thin film

The scanning electron microscopy (SEM) image of the film (Figure 3a) showed the film morphology with evenly distributed small crystallites without any preferred orientation and diffusion grain boundaries. The particles with spherical appearance have good orientation and clearly well-defined grain boundaries. Energy-dispersive X-ray spectroscopy (EDX) analysis of the film shows that the Cu:S ratio is 72.5:27.5. The atomic force microscopy (AFM) image of the film (Figure 3b) shows the growth of closely packed crystallites onto a glass substrate with an average roughness of 11.81 nm (Figure 3c).

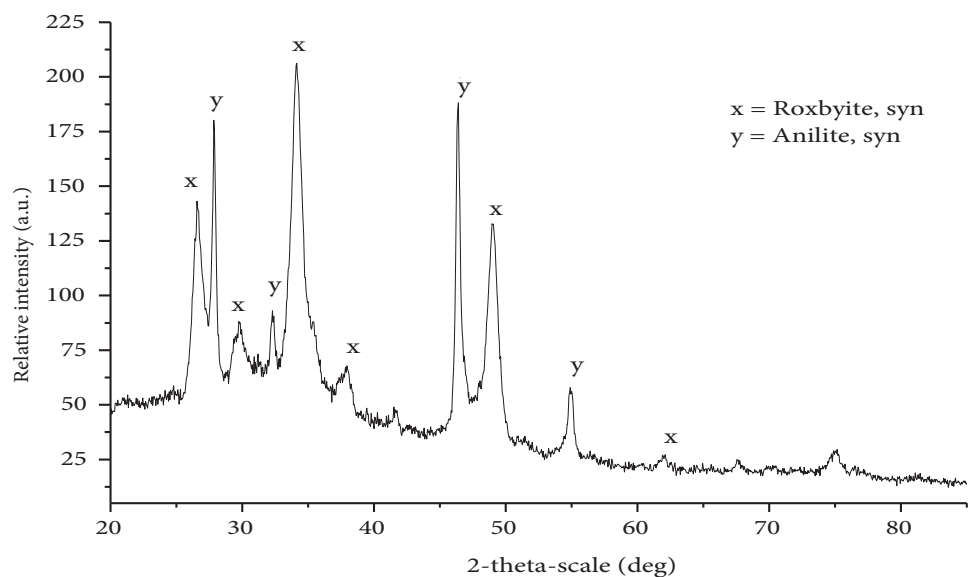


Figure 2. X-ray diffractogram of the copper sulfide thin film obtained from complex (2).

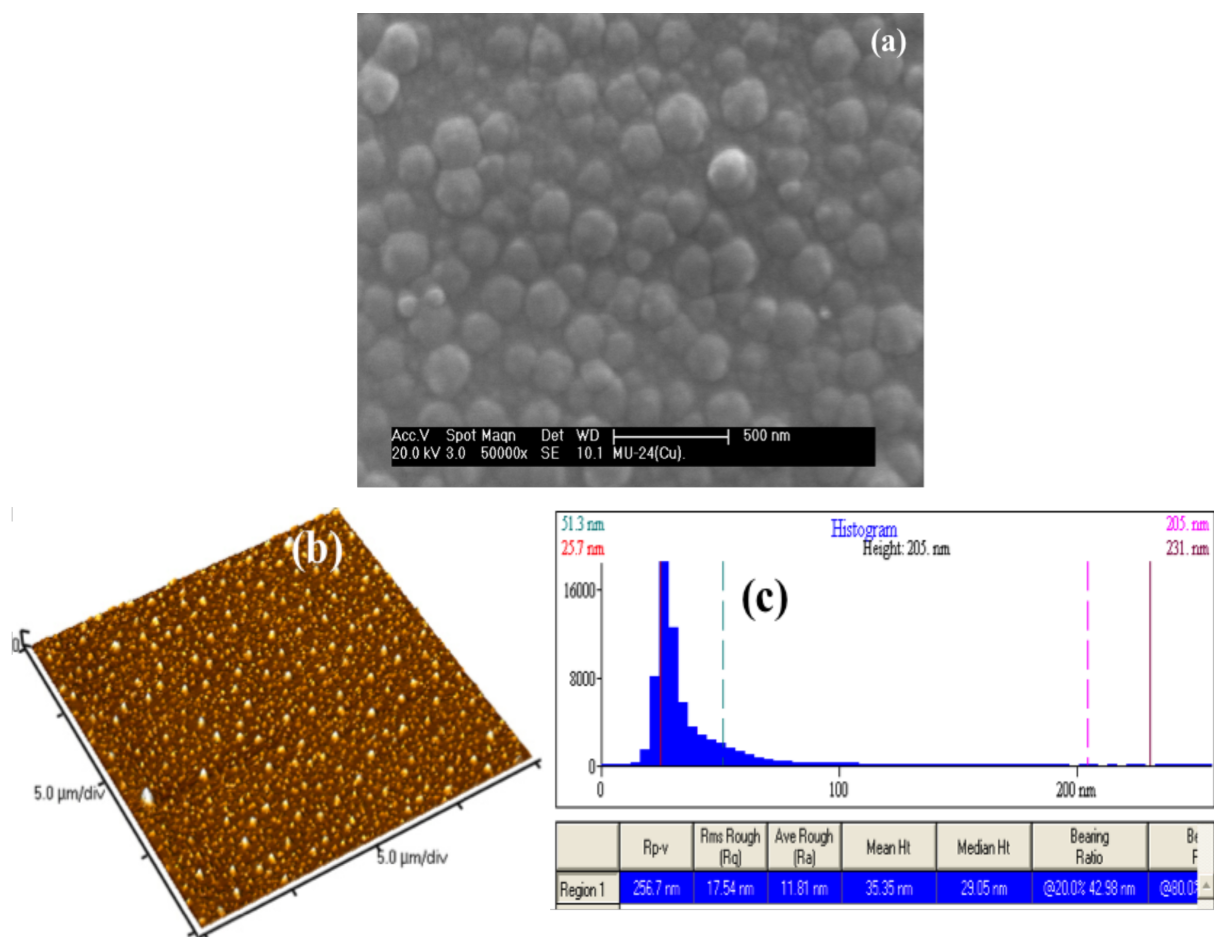


Figure 3. a) SEM image of copper sulfide thin film deposited from 2 at 350 °C, b) AFM image in 3D view of thin film, and c) average roughness and RMS roughness of thin film deposited at 350 °C.

4. Conclusions

We have successfully synthesized an unsymmetrical copper(II) complex of *Bis*[*N*-[ethyl(butyl)carbamothioyl]-3,5-dinitrobenzamide]copper(II). AA-CVD of the copper(II) complex deposited monoclinic roxbyite Cu₇S₄ and orthorhombic anilite Cu₇S₄ phases at 350 °C with spherical crystallites. The composition of the deposited thin film was confirmed by EDX analysis. AFM studies showed that the average roughness of the deposited film was 11.81 nm.

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