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(Z)-2-(pyrrolidin-2-ylidene) thiourea based nickel (II) complex as a single source precursor for the synthesis of NiS nanoparticles and thin films

A. M. Jawore[a], T. Xaba[a,*], M. J. Moloto[b]
[a]*Department of Chemistry, Vaal University of Technology, P/Bag X021, Vanderbijlpark, South Africa*
[b]*Institute for Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa, Florida Science Campus, 1710, South Africa*

Nickel sulfides nanocrystals may be regarded as promising of materials in different research areas such as catalysts, solar cells, and electrode-materials. (Z)-2-(pyrrolidin-2-ylidene) thiourea ligand and (Z)-2-(pyrrolidin-2-ylidene) thiourea based nickel (II) complex have been prepared and utilized as single source molecular precursor for the synthesis of nickel sulfide nanoparticles and thin films. The effect of temperature was studies during the synthetic processes. The synthesized nanomaterials were characterized with various instruments. UV-Vis spectroscopy results of the nanoparticles were red shifting when the reaction temperature was increased whereas the blue shift was observed when the temperature was elevated during the preparation of the NiS thin films with the optical band gap energies ranging from 2.79 eV - 3.56 eV. All the XRD patterns for the NiS thin films confirm the predominance of pure hexagonal phase.

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1. Introduction

The study based on transition metal chalcogenide have received considerable attention due to their applications in different fields. In the family of metal chalcogenides, metal sulfides have demonstrated their interest in electronic properties for technological applications [1-3]. Among transition metal sulfide, nickel sulfide nanomaterials in particular have gained much attention due to their potential application in catalysis and as energy storage [4]. Lately, nickel sulfides have been studied as potential competitors to silicon thin film photovoltaic cells [5]. Nickel sulfides exhibit more complex phases such as α-NiS, β-NiS, NiS_2, Ni_3S_2, Ni_3S_4, Ni_7S_6, and Ni_9S_8, which makes the synthesis of a single-phase nickel sulfide to be more complicated [5-6]. NiS generally exists in two phases, namely hexagonal and rhombohedral [7].

Researchers have intensively synthesized and studied numerous morphologies and shapes of nickel sulfide nanomaterials such as hollowspheres, nanoprisms, nanorods nanospheres, needle-like, flower-like shapes etc, by various methods [8] including precipitation routes [9], solid-state reactions [10], physical vapor and atomic layer depositions [11], electrochemical processes [12], spray pyrolysis [13] or microwave-assisted syntheses [14], chemical bath deposition (CBD) [15], and spin coating method [16]. Among these various methods of preparation, single-source molecular precursor method [4] for the synthesis of nanoparticles and thermal decomposition technique [17] have received significant attention since they provide a better control on shapes, and sizes of the nanomaterials over stoichiometry.

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[*] Corresponding author: thokozanix@vut.ac.za

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In the present work, we report the preparation of (Z)-2-(pyrrolidin-2-ylidene) thiourea ligand and nickel (II) complex, synthesis of TOPO capped nickel sulphide nanoparticles via single source precursor method and the preparation of NiS thin films through thermal composition technique on glass substrates. The effect of reaction temperature was studied during the synthetic processes.

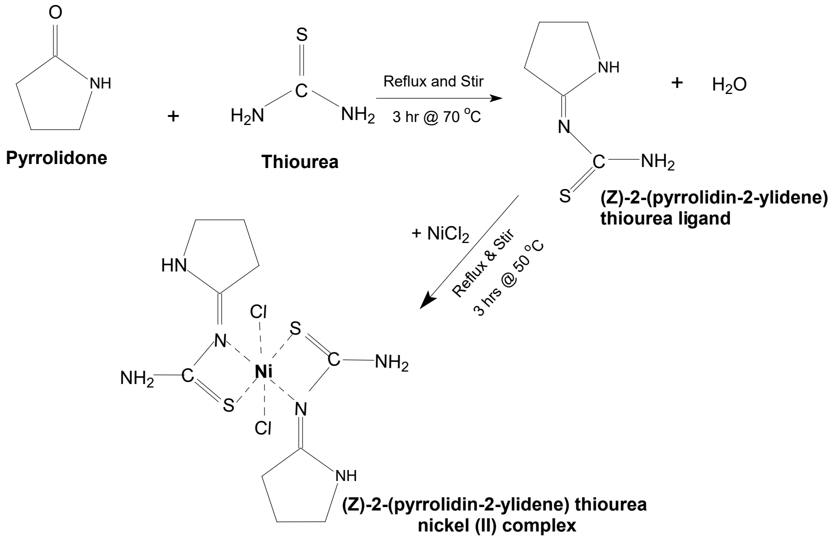
2. Experimental

2.1. Materials

Pyrrolidone, thiourea, nickel chloride hexahydrate, oleylamine, trioctylphosphine oxide (TOPO), ethanol, methanol, toluene, and acetone were reagents from Sigma-Aldrich and were all used without further purification.

2.1.1. Preparation of (Z)-2-(pyrrolidin-2-ylidene) thiourea based Nickel (II) Complex

(Z)-2-(pyrrolidin-2-ylidene) thiourea ligand was prepared according to the reported method [18] which was based on the reaction of pyrrolidone with thiourea. (Z)-2-(pyrrolidin-2-ylidene) thiourea based nickel (II) complex was prepared by mixing thiourea ligand (2 mmol) in an ethanoic solution (20 mL) with an ethanoic solution of nickel chloride (1 mmol). The mixture was refluxed for 3 hours at 50 °C as represented in **Scheme 1** below. It was then cooled at room temperature and the precipitate was filtered, washed with ethanol and then dried in an open air. The complex was obtained as light green powder. Percentage yield: 72.5 %. m.pt. 245 °C. Elemental analysis found (calculated) for $C_{10}H_{18}N_6S_2Cl_2Ni$: C 29.47(28.87) %, H 4.30(4.36) %, N 18.99(20.20) %, and S 15.04(15.41) %.



Scheme 1: Preparation of (Z)-2-(pyrrolidin-2-ylidene) thiourea ligand and (Z)-2-(pyrrolidin-2-ylidene) thiourea based nickel (II) complex

2.1.2. Synthesis of TOPO capped Nickel Sulfide Nanoparticles

Exactly 1.00 mg of Ni(II) complex was dissolved with oleylamine (5 mL) in a small beaker. Trioctylphosphine oxide (TOPO) (5.0 g) was transferred into a 100 mL three necked flask and heated in a nitrogen gas atmosphere to a reaction temperature of 120 °C. The dissolved Ni(II) complex was then injected into hot TOPO and the reaction was allowed to proceed for an hour. The resulting solution was then cooled to about 70 °C and about 20 mL of methanol was added into the flask. The resultant precipitate was separated using centrifugation technique by further addition of methanol.

The product was washed several times with methanol, dried in an open air and characterized. The same procedure was repeated at temperatures of 160 °C and 200 °C instead of 120 °C.

2.1.3. Preparation of Nickel Sulfide Thin Films

The films were deposited on the glass substrate under nitrogen environment in a horizontal hollow reactor. Prior to the experiment, the glass substrates were first cut into equal pieces of 1 x 1.5 cm using a diamond glass cutter. It was then ultrasonically cleaned with acetone for 1 hour and then put to dry. About 0.3 mg of nickel (II) complex was dissolved with 10.00 mL acetone in a small beaker. The precursor solution was then deposited onto the glass substrate that were placed on top of the low heart hot plate covered by foil. About 5–7 glass substrates (1 x 1.5 cm) were placed inside the tube furnace. The substrate was then annealed at various temperatures of 300, 400, and 500 °C for an hour each. The NiS thin films were cooled at room temperature and characterized with various instruments.

2.2. Characterization

UV-1800 Shimadzu spectrophotometer and Gilden Fluorescence were used to measure the optical properties of nickel sulfide nanoparticles and thin films. The NiS nanoparticles were dissolved in toluene and solution was placed in a quartz cuvette with 1 cm path length. XRD patterns of the nanoparticles and thin films were obtained on a Phillips X'Pert chemistry research diffractometer using secondary monochromated Cu Kα radiation ($\lambda = 1.54060$ A°) at 40 Kv/30mA. The data was collected using a glancing angle of incidence detector at an angle of 2 for 2θ values over 10° to 90° in steps of 0.0167 with a scan speed of 0.0452. Transmission electron microscopy (TEM) images were collected using a Tecnai F30 FEG TEM instrument at an accelerating voltage of 300 kV. TEM samples were prepared by placing few drops of NiS nanoparticles dissolved in toluene on a carbon copper grids and the SEM analysis for thin films were performed using a Philips XL 30FEG.

3. Results and discussion

3.1. FTIR Spectroscopy and Thermogravimetric Analysis

The FTIR measurements for the ligand and nickel (II) complex were conducted in the scan range between 400 cm^{-1} to 4000 cm^{-1} at room temperature. Figure 1(a) shows the FTIR of (Z)-2-(pyrrolidin-2-ylidene) thiourea ligand and (Z)-2-(pyrrolidin-2-ylidene) thiourea based nickel (II) complex. The peaks at 3440 - 3150 cm^{-1} and 3305 – 3100 cm^{-1} were assigned to O–H stretching vibration due to ethanol for washing. A peak at 3080 cm^{-1} was observed and was associated with C-H stretch. The N–H bending were observed at the regions between 1650 and 1610 cm^{-1}. The N–C-S functional group was located at 1470 cm^{-1} and C=S peak was observed at 1080 cm^{-1} and N=H stretching was located at 1010 cm^{-1}. A peak at 466 cm^{-1} was observed which corresponds to the metal sulfide (Ni-S).

Figure 1(b) shows the TGA graphs of (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex. The (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex displays the first step decomposition at 191 – 226 °C which might be attribute to C – N, C – C and C – H. The second step shows the last decomposition at 328 - 562 °C with final residue 13% which attribute to loss Ni–N and the last decomposition between at 568 - 681 °C may be associated with the other organic parts of the compound [19].

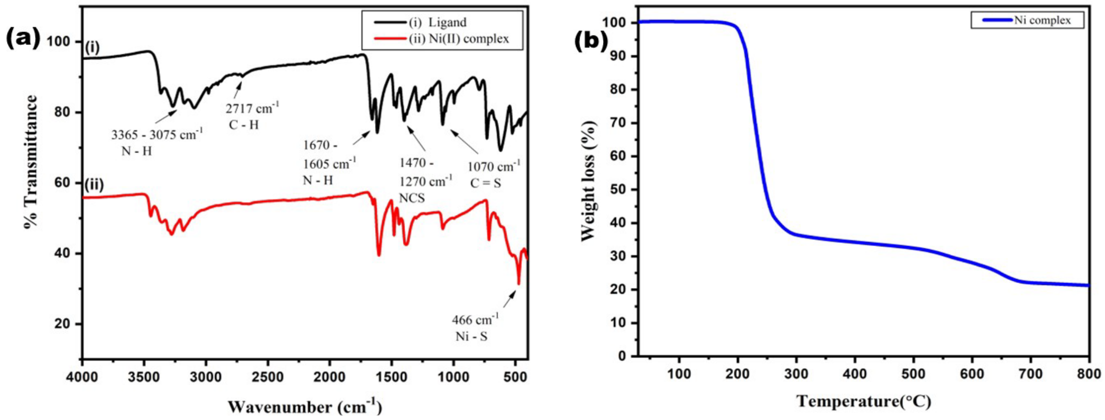


Fig. 1. FTIR Spectra of (Z)-2-(pyrrolidin-2-ylidene) thiourea ligand & nickel (II) complex (a) and TGA curve for nickel (II) complex (b).

3.2. UV-Vis and Emission spectroscopy of the TOPO capped NiS Nanoparticles

Figure 2(a) shows UV-Vis absorption of TOPO capped nickel sulfide nanoparticles synthesized from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 120 ºC, 160 ºC, and 200 ºC with the absorption wavelengths of 309, 311, and 418 nm, respectively. All the TOPO capped nickel sulfide nanoparticles were blue-shifted from their bulk nickel sulfide material (495 nm) [20].

The emission spectra of the TOPO capped nickel sulfide nanoparticles is represented in Figure 2(b) below. The emission spectra showed two peaks for the TOPO capped NiS nanoparticles prepared at 120 ºC, 160 ºC, and 200 ºC. The two peaks maxima were located at 408 nm & 433 nm, 409 nm & 433 nm, and 409 nm & 433 nm. The double narrow emission peaks serve as an indication of the monodispersed and small size particles.

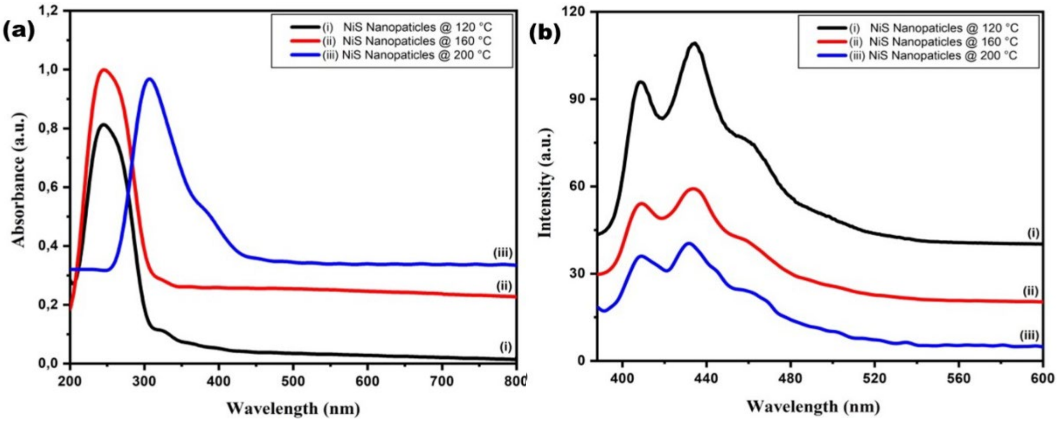


Fig. 2. UV–Vis (a) and photoluminescence (b) spectra of the TOPO capped NiS nanoparticles synthesized from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 120 ℃ (i), 160 ℃ (ii), and 200 ℃ (iii).

3.3. X-Ray Diffraction patterns of the TOPO capped NiS Nanoparticles

The X-ray diffraction of the TOPO capped nickel sulfide nanoparticles synthesized at different temperatures of 120º, 160º, and 200º are shown in Figure 3 below. The TOPO capped NiS nanoparticles prepared at lower temperatures of 120º and 160º exhibited peaks that agree well with the standard pattern of rhombohedral crystalline NiS (JCPDS 12-0041) [21]. The nickel sulfide nanoparticles that were synthesized at higher temperature of 200º exhibited peaks at 30.33º (100), 34.90º (101), 46.37º (102), and 53.90º (110) that correspond to the α-NiS hexagonal phase with the

JCPDS card number 00-002-1280 which is similar to the previously reported results [22]. The peak that is located around 20° may be attributed to the capping molecule.

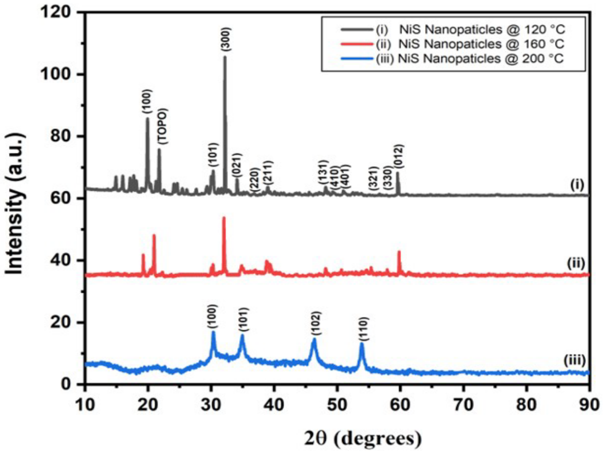


Fig. 3. XRD patterns of the TOPO capped NiS nanoparticles synthesized from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 120 ºC (i), 160 ºC (ii), and 200 ºC (iii).

3.4. Transmission electron microscopy (TEM) images of the TOPO capped NiS Nanoparticles

Figure 4 shows TEM morphology of the synthesized TOPO capped nickel sulfide nanoparticles at different temperatures. All the nickel sulfide nanoparticles showed spherical and dot-like structured particles with the average particle sizes of 1.84 nm, 2.52 nm, and 2.82 nm.

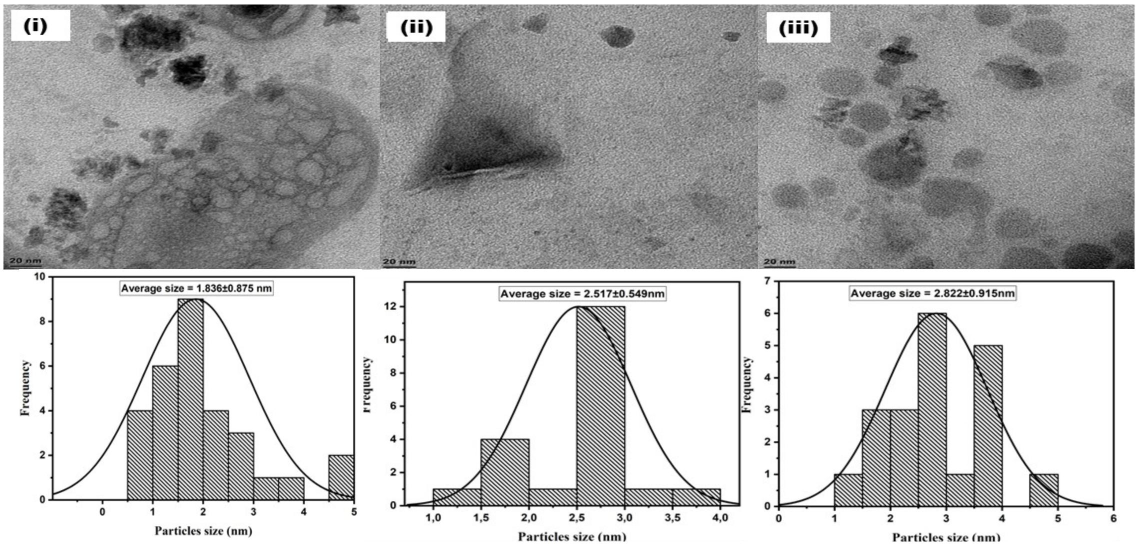


Fig. 4. TEM image of the TOPO capped NiS nanoparticles synthesized from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 120 ºC (i) 160 ºC (ii), and 200 ºC (iii).

3.5. UV-Vis spectroscopy and Tauc Plot of the NiS Thin Films

UV–Vis is spectra of the prepared nickel sulfide thin films from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex is represented by Figure 5(a) below. The absorption spectra exhibit of the prepared NiS thin films at the temperature of 300 °C, 400 °C and 500 °C show the maximum wavelengths with their corresponding band edges at 327 nm, 328 nm, and 330 nm. The band was projected by Tauc's relationship [23] between the optical absorption coefficient, α, the photon energy (hν), constant (*A*) and the direct band gap energy (Eg) as shown below in eqn. (1):

$$\alpha h\nu = A(h\nu - E_g)^n \tag{1}$$

where n = 1/2 for direct transitions and n = 2 for indirect transition. The Tauc plot in Fig. 5(b) was achieved by plotting (αhν)2 against photon energy (hν) and extrapolating the linear segment of the curve to absorption coefficient equal to zero. It shows the energy band gab of 2.79, 3.24, and 3.56 eV for the NiS thin films that were prepared at different temperatures of 300 °C, 400 °C and 500 °C.

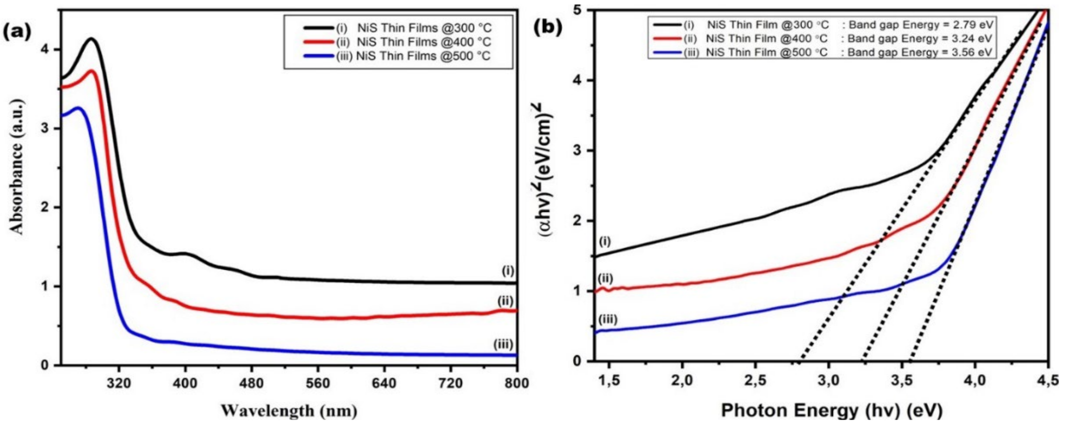


Fig. 5. UV-Vis spectra (a) and Tauc plot (b) of NiS thin film deposited from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 300 ℃ (i), 400 ℃ (ii), and 500 ℃ (iii).

3.6. Emission spectroscopy and X-ray Diffraction patterns of the NiS Thin Films

Figure 6(a) shows the emission spectra of the prepared nickel sulfide thin films from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at different decomposition temperatures with excitation wavelength 370 nm. At deposition temperatures 300 °C, 400 °C and 500 °C, all the prepared NiS thin films showed two emission maxima peaks at 415 nm & 433 nm. The observed narrow peaks signify monodispersed films on the glass substrates.

Figure 6(b) shows the XRD patterns of nickel sulfide thin films prepared at various reaction temperatures. All the XRD patterns of the prepared NiS thin films revealed the peaks at about 30.23°, 34.92°, 45.73° and 53,75° associated with (100), (101), (102), and (110) planes that correspond to the pure hexagonal phase α-NiS (JCDD PDF: 01-075-0613).

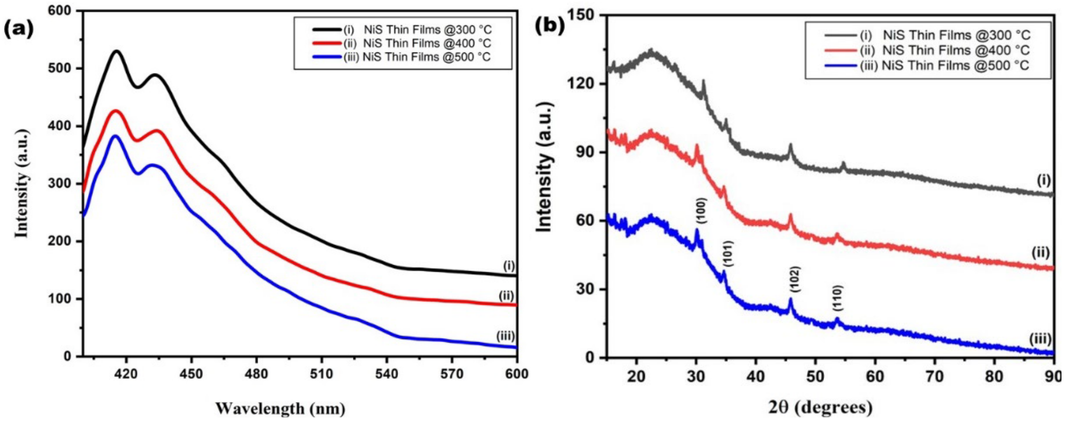


Fig. 6. Emission spectra (a) and XRD patterns (b) of the NiS thin film deposited from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 300 ℃ (i) 400 ℃ (ii), and 500 ℃ (iii).

3.7. Scanning Electron Microscopy (SEM) images of the NiS Thin Films

Figure 7 shows the SEM micrograms of nickel sulfide thin films prepared at different temperatures. SEM images of thin films prepared at 300 °C and 400 °C showed irregular structured particles while well distributed and uniform particles that consist of spherical grains like particles were observed at the NiS thin films prepared at higher temperature of 500 °C.

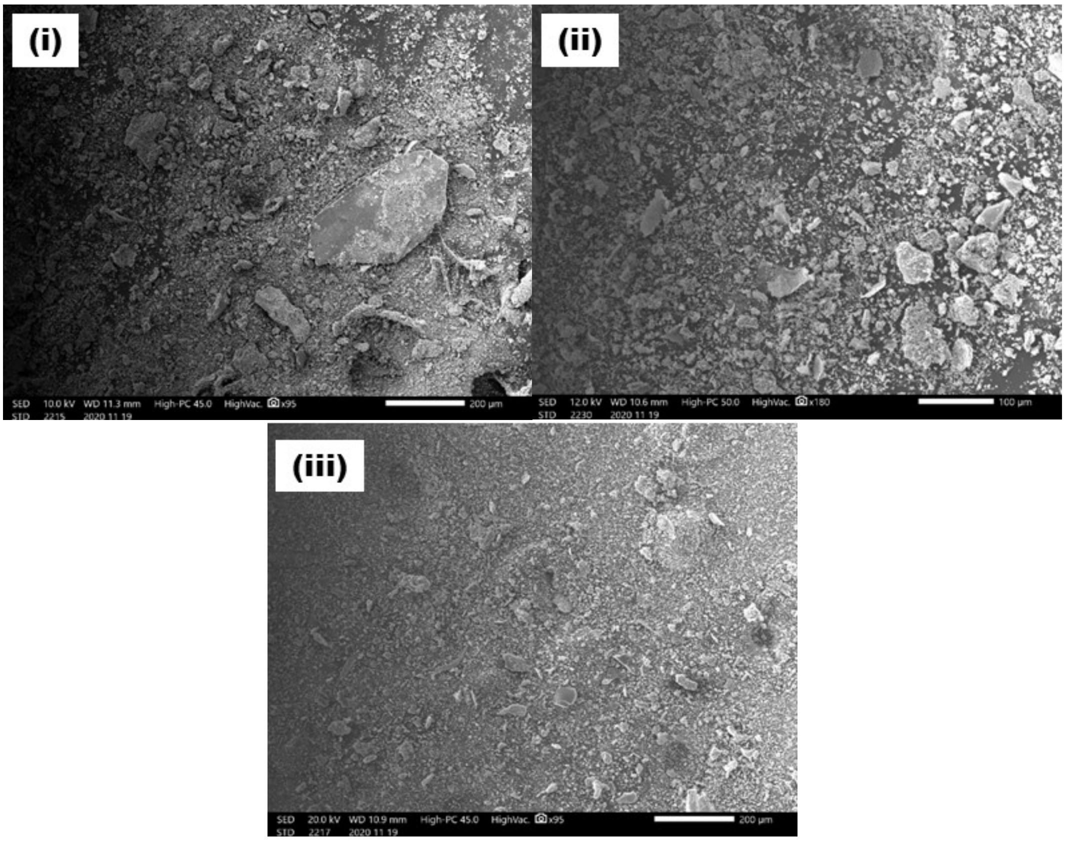


Fig. 7. SEM images of NiS thin film deposited from (Z)-2-(pyrrolidin-2-ylidene) thiourea nickel (II) complex at 300 ℃ (i) 400 ℃ (ii), and 500 ℃ (iii).

4. Conclusion

The preparation of (Z)-2-(pyrrolidin-2-ylidene) thiourea ligand and (Z)-2-(pyrrolidin-2-ylidene) thiourea based nickel (II) complex has been accomplished. The nickel complex was used as a precursor to synthesize NiS nanoparticles and thin films. The optical absorption measurements of the prepared nanomaterials showed the blue shift compared to that of the bulk materials. TEM images revealed that the particle sizes were increasing when the reaction temperature was increased. The band gab energies of the prepared NiS thin films were increasing with the increase in reaction temperature. The SEM micrograms of the thin films were revealing irregular structured particles at lower temperatures whereas spherical particles were observed at higher temperatures.

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