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Growth and characterization of semiconducting nickel sulfide nanocrystals from air-stable single-source metal organic precursors

Sohail Saeed^{1,2*} and Naghmana Rashid¹

Abstract: Three symmetrical and unsymmetrical nickel(II) complexes [*cis*-(C₃H₇)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Ni(II), [*cis*-(C₄H₉)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Ni(II), and [*cis*-(Hex)(Me)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Ni(II) were synthesized and characterized by FTIR spectroscopy, elemental analysis, and mass spectrometry. These metal complexes have been used as single-source precursors for the preparation of semiconducting nickel sulfide nanocrystals. Rapid injection of metal complexes into oleylamine at 230°C, followed by immediate cooling, led to the formation of irregular-shaped 20–170-nm nickel sulfide nanocrystals. The deposited nickel sulfide nanocrystals were characterized by X-ray powder diffraction and transmission electron microscopy.

Subjects: Inorganic Chemistry; Materials Science; Semiconductors

Keywords: nanomaterials; nickel sulfide nanocrystals; X-ray powder diffraction (p-XRD); transmission electron microscopy (TEM); symmetrical and unsymmetrical nickel(II) complexes; single-source precursors

ABOUT THE AUTHORS

Sohail Saeed has completed his MSc in Organic Chemistry from The University of Punjab, Lahore, and PhD in Organic Chemistry in 2013 from Allama Iqbal Open University, Islamabad, Pakistan. His current research interest focuses on the deposition of semiconducting nanostructured metal sulfide thin films from single-source precursors, medicinal chemistry, nanocomposites, and heterocyclic chemistry. He has published more than 60 research articles in well-reputed international journals. He is presently working as a Deputy Project Director in CESAT, Islamabad, Pakistan.

Naghmana Rashid did her MSc and MPhil in 1984 and 1986 from Quaid-e-Azam University Islamabad, Pakistan in Organic Chemistry under the supervision of Mashooda Hasan and Rashid Iqbal (late), respectively. Currently, she is the dean of Sciences and Chairperson of the Department of Chemistry, Allama Iqbal Open University, Islamabad, Pakistan. Major research interests are chiral synthesis, heterocyclic synthesis, materials, medicinal and pesticides chemistry.

PUBLIC INTEREST STATEMENT

Development of semiconducting metal sulfide nanocrystals and thin films from single-source precursors is an emerging field for the researchers working in the area of nanomaterials. There are many physical and chemical techniques for the preparation of metal sulfide nanocrystals from metal-organic single-source precursors. Production of metal sulfide nanocrystals from single-source precursors through colloidal thermolysis using oleylamine as surfactant is a best method to achieve the controlled size of nanoparticles. Semiconducting nanostructured nickel sulfide thin films are used in the field of photovoltaic applications.



Sohail Saeed

1. Introduction

Crystalline metal sulfides as a typical and important group of semiconductors have attracted extensive investigation due to their unique optical, magnetic, and electrical properties and the intriguing prospects for developments in photovoltaic solar cells, biological labeling, and medical diagnostics. (Shen et al., 2011). 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 (Monajjemi, Baei, & Mollaamin, 2008). 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, nickel, and copper sulfide (Monajjemi, Mahdavian, Mollaamin, & Khaleghian, 2009; Zare, Darouleh, Mollaamin, & Monajjemi, 2011). The properties and application of semiconducting nanostructured materials are extensively depend on their crystal phase, size, composition, and shape, as well as the processing technique for the production of highly tuned nanocrystals (Sun & Xia, 2002).

The phase diagram of the Ni-S system is more complex than that of the Fe or Co sulfides. In this system, many crystalline phases and stoichiometries have been reported including $\text{Ni}_{3+x}\text{S}_{2x}$, Ni_3S_2 , $\text{Ni}_{4+x}\text{S}_{2x}$, Ni_6S_5 , Ni_7S_6 , Ni_9S_8 , NiS, Ni_3S_4 , and NiS_2 (Barry & Ford, 2001; Swain, 1981). Some compounds, e.g. NiS and NiS_2 , have been studied extensively, while for others, only more limited information is available. NiS_2 (Vaesite) is a p-type semiconductor with a band gap of 0.5 eV (Sartale & Lokhande, 2001). It is potentially useful in: photo electrochemical solar cells (Sharon, Tamizhmani, Levy-Clement, & Rioux, 1989; Zainal, Saravanan, & Mien, 2005), IR detectors (Oyama, 2003), catalysis (Mane & Lokhande, 2000), and sensors (Cheon, Talaga, & Zink, 1997). It is also used as a hydrodesulfuration catalyst and as a cathode material in rechargeable lithium batteries (Cheon et al., 1997). Recently, Saeed, Rashid, Hussain, et al. (2013) have used nickel(II) complexes of thiourea derivatives as single-source precursors for the deposition of nickel sulfide nanoparticles and nanocrystals).

There is a long-term ambition for electricity generation from solar energy and potentially NCs solar cells with low fabrication costs are an exciting prospect. Our team has focused on synthesis, characterization, crystal structures, biological activities, and material applications of new thiourea derivatives and their metal complexes (Saeed, Rashid, & Ahmad, 2013; Saeed, Rashid, Jones, Ali, & Hussain, 2010; Saeed, Rashid, Jones, & Tahir, 2011; Saeed & Wong, 2012). In this communication, we have synthesized three symmetrical and unsymmetrical nickel(II) metal complexes [*cis*-(C_3H_7)₂NC(S)NC(O) C_6H_3 (3,5- NO_2)₂] $\text{Ni}(\text{II})$, [*cis*-(C_4H_9)₂NC(S)NC(O) C_6H_3 (3,5- NO_2)₂] $\text{Ni}(\text{II})$, and [*cis*-(Hex)(Me)₂NC(S)NC(O) C_6H_3 (3,5- NO_2)₂] $\text{Ni}(\text{II})$ and characterized each by spectroscopic techniques. In addition, the metal complexes have been used as single-source precursors for the deposition of nickel sulfide nanocrystals by colloidal thermolysis.

2. Experimental section

2.1 Materials and physical measurements

Analytical grade 3,5-dinitrobenzoyl chloride ($\geq 98.0\%$), di-n-butylamine (99%), di-n-propylamine (99%), sodium thiocyanate (99%), N-hexylmethylamine ($\geq 98.0\%$), oleylamine-approx.C18 content 80–90%, nickel(II) acetate tetrahydrate (99%), and tetrabutylammonium bromide (TBAB) ($\geq 98\%$) were purchased from Sigma-Aldrich. Analytical grade solvents such as tetrahydrofuran (THF), acetonitrile, n-hexane, dichloromethane, ethanol, methanol, ethyl acetate, and others were purchased from Sigma-Aldrich and Riedel-de Haën (Germany), whereas ethanol and acetone were dried using standard procedures (Perrin, Armarego, & Perrin, 1988). All manipulations were carried out in air except for the thermolysis experimentations. The synthesis of nickel sulfide nanocrystals was carried out under N_2 inert atmosphere. The symmetrical and unsymmetrical ligands [$(\text{C}_3\text{H}_7)_2\text{NC(S)NC(O)C}_6\text{H}_3(\text{NO}_2)_2$ -3,5] (**1a**), [$(\text{C}_4\text{H}_9)_2\text{NC(S)NC(O)C}_6\text{H}_3(\text{NO}_2)_2$ -3,5] (**1b**), and [(Hex)(Me)₂NC(S)NC(O) C_6H_3 (NO_2)₂-3,5] (**1c**) were synthesized and recrystallized according to literature methods (Saeed et al., 2010). Elemental analysis of the ligands and complexes was performed by Flash 2000 elemental analyzer. Obtained results were within 0.4% of the theoretical values. Infrared spectra were recorded on a Specac single reflectance attenuated total

reflectance instrument (4,000–400 cm^{-1} , resolution 4 cm^{-1}). Atmospheric pressure chemical ionization mass spectrometry (MS-APCI) of the ligands and nickel complexes (MS-APCI) 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 the Barloworld SMP10 melting point apparatus. Thermal stability of the nickel complexes was studied by thermogravimetry in an inert atmosphere, at sample heating rate of 10°C/min, with a DuPont 2000 ATG. X-ray powder diffraction studies were performed on an Xpert diffractometer using Cu-K α 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 (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. Transmission electron microscopic images were collected on a Philips CM200 transmission electron microscope using an accelerating voltage of 200 kV.

2.2. Preparation of the ligands

2.2.1. Synthesis of $[(\text{C}_3\text{H}_7)_2\text{NC}(\text{S})\text{NC}(\text{O})\text{C}_6\text{H}_4\text{-4-NO}_2]$ (**1a**)

A solution of 3,5-dinitrobenzoyl chloride (0.01 mol) in anhydrous acetone (80 mL) and 0.3 mol % of tetrabutylammonium bromide (TBAB) in acetone was added dropwise to a suspension of sodium thiocyanate in acetone (50 mL) and the reaction mixture was refluxed for 45 min. After cooling to room temperature, 0.01 mol of a solution of di-n-propylamine in acetone (25 mL) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into five times its volume of cold water, whereupon the acylthiourea precipitated. The solid product was washed with water and purified by recrystallization from an ethanol-dichloromethane mixture (1:2). Light-yellow prisms. M.p.: 134–135°C. Yield: 3.3 g (82%). IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3,147 (NH), 2,921, 2,867 (C–H), 1,688 (C=O), 1,256 (C=S). ^1H NMR (400 MHz, CDCl_3) in δ (ppm) and J (Hz): δ 9.10 (t, 1H, $J = 1.8$), 8.86 (d, 2H, $J = 1.8$), 8.35 (bs, 1H, CONH), 3.95 (t, 2H, N– CH_2), 3.52 (t, 2H, N– CH_2), 1.85 (m, 2H, $-\text{CH}_2-$), 1.68 (m, 2H, $-\text{CH}_2-$), 1.04 (t, 3H, CH_3), 0.92 (t, 3H, CH_3). 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, 47.53; H, 5.17; N, 15.75; S, 9.03.

2.2.2. Synthesis of $[(\text{C}_4\text{H}_9)_2\text{NC}(\text{S})\text{NC}(\text{O})\text{C}_6\text{H}_4\text{-4-NO}_2]$ (**1b**)

Ligand (**1b**) was synthesized by the method described for ligand (**1a**) using di-n-butylamine. Blackish brown in semi-solid state. M.p.: 92–93°C. Yield: 3.4 g (78%). IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3,206 (NH), 2,955, 2,847 (C–H), 1,685 (C=O), 1,261 (C=S). ^1H NMR (400 MHz, CDCl_3) in δ (ppm) and J (Hz): δ 9.10 (t, 1H, $J = 1.8$), 8.85 (d, 2H, $J = 1.8$), 8.38 (bs, 1H, CONH), 3.97 (t, 2H, N– CH_2), 3.52 (t, 2H, N– CH_2), 1.83 (m, 2H, $-\text{CH}_2-$), 1.68 (m, 2H, $-\text{CH}_2-$), 1.46 (m, 2H, $-\text{CH}_2-$), 1.32 (m, 2H, $-\text{CH}_2-$), 1.01 (t, 3H, CH_3), 0.92 (t, 3H, CH_3). Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_4\text{O}_5\text{S}$: C, 50.25; H, 5.80; N, 14.65; S, 8.38. Found: C, 50.23; H, 5.83; N, 14.67; S, 8.35.

2.2.3. Synthesis of $[(\text{Hex})(\text{Me})\text{NC}(\text{S})\text{NC}(\text{O})\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-3,5}]$ (**1c**)

Ligand (**1c**) was synthesized by the method described for ligand (**1a**) using *N*-hexylmethylamine. Light yellow in semi-solid state. M.p.: 98–99°C. Yield: 3.3 g (77%). IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3,176 (NH), 2,959, 2,877 (C–H), 1,685 (C=O), 1,262 (C=S). ^1H 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, CONH), 3.90 (t, 2H, N– CH_2), 3.01 (s, 3H, CH_3), 2.57 (m, 2H, $-\text{CH}_2-$), 1.83 (m, 2H, $-\text{CH}_2-$), 1.66 (m, 2H, $-\text{CH}_2-$), 1.27 (m, 2H, $-\text{CH}_2-$), 0.90 (t, 3H, CH_3). Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$: 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.

2.3. Synthesis of nickel(II) complexes

2.3.1. Synthesis of $[\text{cis}-(\text{C}_3\text{H}_7)_2\text{NC}(\text{S})\text{NC}(\text{O})\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-3,5}]_2\text{Ni}(\text{II})$ (**2a**)

A solution of nickel acetate (0.005 mol) in methanol (35 cm^3) was added dropwise to a solution of the ligand (**1a**) in a 1:2 ratio with a small excess of ligand (**1a**) in ethanol (35 cm^3) 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). Brown. Yield: 3.8 g (81%). IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2,928, 2,856 (Ar–H), 1,501 (C–O), 1,536 (C–N), 1,128 (C–S); ^1H NMR (400 MHz, CDCl_3) in δ (ppm) and J (Hz):

δ 9.06 (t, 2H, Ar-H), 8.87 (d, 4H, Ar-H), 3.80 (m, 8H, -CH₂), 1.59 (m, 8H, -CH₂), 0.96 (t, 12H, CH₃). Anal. Calcd for C₂₈H₃₄N₈O₁₀S₂Ni: C, 43.94; H, 4.48; N, 14.64; S, 8.38; Ni, 7.67. Found: C, 43.64; H, 4.29; N, 14.48; S, 8.35; Ni, 7.41. Mass (MS-APCI) (major fragments, m/z): 765[M⁺, C₂₈H₃₄N₈O₁₀S₂Ni], 353[C₁₄H₁₇N₄O₅S].

2.3.2. Synthesis of *[cis-(C₆H₉)₂NC(S)NC(O)C₆H₃(NO₂)₂-3,5]₂Ni(II) (2b)*

Complex (2b) was synthesized by the method described for complex (2a). Quantities used were 3.82 g (0.01 mol) ligand (1b) and 1.24 g (0.005 mol) nickel acetate tetrahydrate in ethanol. Brownish golden. Yield: 4.3 g (86%). IR (ν_{\max} /cm⁻¹): 2,929, 2,857(Ar-H), 1,507(C-O), 1,534 (C-N), 1,127(C-S); ¹H NMR (400 MHz, CDCl₃) in δ (ppm) and *J* (Hz): δ 9.08 (t, 1H, Ar-H), 8.82 (d, 2H, Ar-H), 3.71 (m, 8H, N-CH₂), 1.73 (m, 8H, -CH₂-), 1.45 (m, 8H, -CH₂-), 0.96 (m, 12H, CH₃). Anal. Calcd for C₃₂H₄₂N₈O₁₀S₂Ni: C, 46.78; H, 5.15; N, 13.64; S, 7.81; Ni, 7.14. Found: C, 46.86; H, 5.07; N, 13.64; S, 7.79; Ni, 6.70. Mass (MS-APCI) (major fragments, m/z): 825[M⁺, C₃₂H₄₂N₈O₁₀S₂Ni].

2.3.3. Synthesis of *[cis-(Hex)(Me)NC(S)NC(O)C₆H₃(NO₂)₂-3,5]₂Ni(II) (2c)*

Complex (2c) was synthesized by the method described for complex (2a). Quantities used were 3.68 g (0.01 mol) ligand (1c) and 1.24 g (0.005 mol) nickel acetate tetrahydrate in ethanol. Yellowish golden. M.p.: 110–111°C. Yield: 3.3 g (68%). IR (ν_{\max} /cm⁻¹): 2,927, 2,855(Ar-H), 1,502(C-O), 1,537 (C-N), 1,153(C-S); ¹H NMR (400 MHz, CDCl₃) in δ (ppm) and *J* (Hz): δ 9.09 (t, 2H, Ar-H), 8.77 (d, 4H, Ar-H), 3.84 (m, 4H, N-CH₂), 3.04 (s, 6H, CH₃), 2.59 (m, 4H, -CH₂-), 1.84 (m, 4H, -CH₂-), 1.62 (m, 4H, -CH₂-), 1.31 (m, 4H, -CH₂-), 0.94 (t, 6H, CH₃). Anal. Calcd for C₃₀H₃₈N₈O₁₀S₂Ni: C, 45.41; H, 4.83; N, 14.12; S, 8.08; Ni, 7.40. Found: C, 44.62; H, 4.42; N, 14.07; S, 8.07; Ni, 7.24. Mass (MS-APCI) (major fragment, m/z): 793[M⁺, C₃₀H₃₈N₈O₁₀S₂Ni].

2.4. Deposition of nickel sulfide nanocrystals

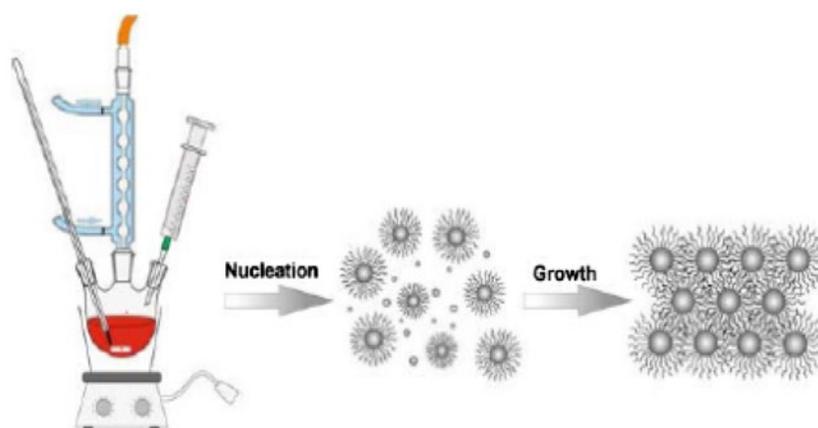
Nickel sulfide nanocrystals were prepared by pyrolyzing the nickel complex as a precursor in oleylamine (Figure 1). In a typical reaction, 15 mL of oleylamine was refluxed under vacuum at 90°C for 45 min, and then it was purged by nitrogen gas for 30 min, at same temperature. Then 0.3 g of precursor was added into hot oleylamine and the reaction temperature was slowly increased to a desired point (170 and 230°C). The temperature was maintained for one hour and the mixture was allowed to cool to room temperature. Addition of 30-mL methanol produced a black precipitate which was separated by centrifugation. The black residue was washed twice by methanol and redispersed in toluene or hexane for further characterizations.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The symmetrical and unsymmetrical acylthiourea derivatives and their nickel(II) complexes were synthesized according to the reported procedure (Arslan, Flörke, Külcü, & Emen, 2006; Zhang, Pang, Cao, & Wei, 2008). The solid-state IR spectra of the thiourea derivatives and the metal complexes in

Figure 1. Experimental setup for colloidal synthesis of nanocrystals (NCs).



the region 4,000–400 cm^{-1} were compared and assigned on careful comparison. Tentative assignments are made according to their literature (Mansuroglu, Arslan, Flörke, & Külcü, 2008). *N, N'*-disubstituted thioureas behave both as monodentate and bidentate ligands, depending upon the reaction conditions. The characteristic bands of *N, N'*-disubstituted thioureas are 3,226 (NH), 2,867, 2,944 Ph (CH), 1,671(C=O), and 1,259 (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 nickel atom.

As is well known, acyothiureas usually act as bidentate ligands to transition metal ions through the acyl oxygen and sulfur atoms (Yuan, Wang, Gimeno, Laguna, & Jones, 2001). The FTIR spectra of the complexes showed significant changes when compared with the FTIR spectra of the corresponding ligands. The IR spectra of the complexes showed absorption bands at $\nu_{\text{max}}/\text{cm}^{-1}$: 2,847–2,959 Ph (CH), 1,501–1,507 (C–O), 1,534–1,537 (C–N), and 1,128–1,153 (C–S). The most striking changes are the N–H stretching frequency at 3,226 cm^{-1} in the free ligands, which disappears completely, in agreement with both ligands and complex structures and with the complexation reaction. This indicates that the loss of the proton comes from originally bonded nitrogen atom of the (NH–CO) amide group. Another striking change is observed with the carbonyl stretching vibrations. The vibrational frequencies due to the carbonyl (1,685–1,688 cm^{-1}) group in the free ligands are shifted toward lower frequencies upon complexation, confirming that the ligand is coordinated to the nickel(II) ion through the oxygen and sulfur donor atoms (Domínguez et al., 2002). A comparative absorption pattern of the complex with the values of the free ligand demonstrates that the coordination of an acylthiourea ligand to a nickel atom has a significant effect on $\nu(\text{NH})$, $\nu(\text{CO})$, and $\nu(\text{CS})$ frequencies.

The ^1H NMR data for the synthesized symmetrical and unsymmetrical *N, N'*-disubstituted thiourea compounds show that the NH hydrogen resonates considerably downfield from other resonances in the spectrum. The proton chemical shifts are found to be 8.85 for free NH protons and the aromatic protons appear downfield between 7.35 and 8.32 ppm. It has also been observed that coordinating or highly polar solvents like DMSO-*d*₆ have profound effects on the free NH protons chemical shifts and appear more downfield as compared with the solvents like C_6D_6 , CDCl_3 and CD_2Cl_2 . This shift can be attributed to the possible hydrogen bonding between NH and the sulfoxide (S=O) moiety. ^1H NMR data for the metal complex describe the existence of aromatic protons in the range of 8.28–8.01 ppm as reported earlier (Arslan & Külcü, 2003). The resonances due to NH group of the CONH moiety in ligands (**1a–c**) are completely disappeared in complexes (**2a–c**). This indicates that the loss of the proton was originally bonded to the nitrogen atom of the (NH–CO) amide group in the ligands and confirms the formation of the nickel complexes. Thus, all the characteristic chemical shifts were identified by their intensity and multiplicity patterns.

3.2. XRD and TEM characterization of nickel sulfide nanocrystals deposited from precursors (**2a–c**)

The XRD pattern for the NiS nanocrystals synthesized from precursor (**2a**) is shown in Figure 2(a). The synthesis of nickel sulfide nanocrystals was carried out at 170 and 230°C. No deposition was obtained below 170°C as the material was almost in non-crystalline form. At 230°C, the XRD pattern of NiS nanocrystals shows diffractions of hexagonal NiS and the space group P63/mmc with major diffraction peaks of (1 0 0), (1 0 1), (1 0 2) and (1 1 0) planes (ICDD: 075-0613). The TEM image (Figure 3(a)) shows the particles are in spherical and irregular shapes. There was a certain degree of agglomeration and size of the particles could be approximated to 20–25 nm in diameter. The XRD pattern for the $\text{Ni}_{17}\text{S}_{18}$ nanocrystals synthesized from precursor (**2b**) is shown in Figure 2(b). The synthesis of nickel sulfide nanocrystals was carried out at 170 and 230°C. The material was almost in non-crystalline form at this temperature. At 230°C, the XRD pattern of nickel sulfide nanocrystals shows diffractions of hexagonal $\text{Ni}_{17}\text{S}_{18}$ and the space group P3121 (1 5 2) with major diffraction peaks of (0 2 4), (0 3 3), (3 0 6), and (3 3 0) planes (ICDD: 04-007-1010). As it is clear from the TEM image (Figure 3(b)), the particles are conical in shape having 20–75-nm length. The XRD pattern for the NiS nanocrystals synthesized from precursor (**2c**) is shown in Figure 2(c). The reaction conditions for deposition of nickel sulfide nanocrystals were at 170 and 230°C.

Figure 2. XRD pattern of nickel sulfide nanocrystals deposited from precursors (2a–c).

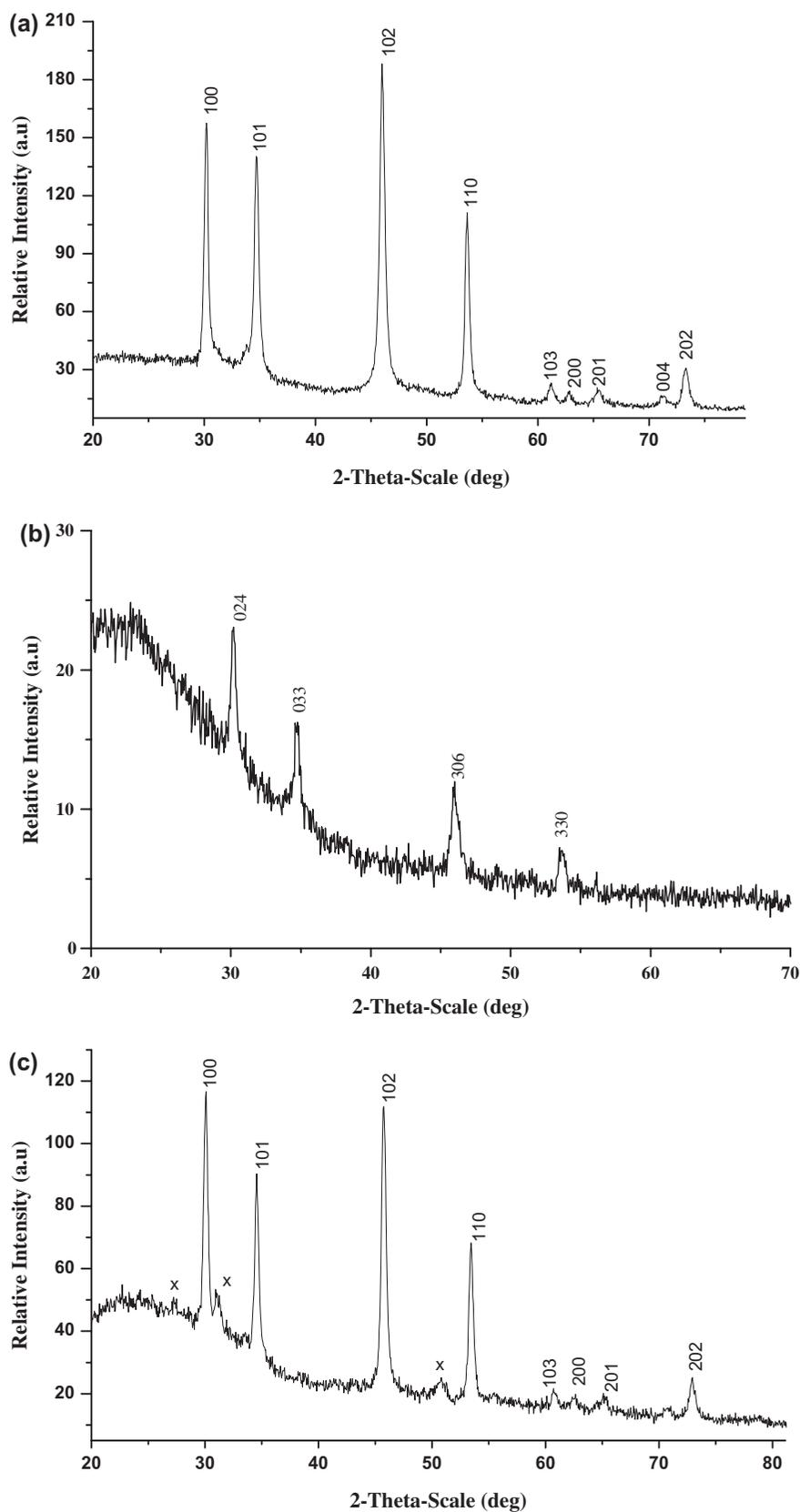
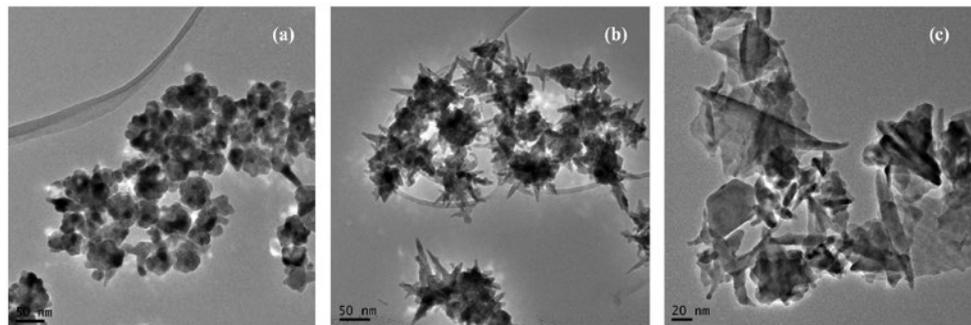


Figure 3. TEM images of precursors (2a–c).



At 230°C, the XRD pattern of NiS nanocrystals shows diffractions of hexagonal NiS and the space group P63/mmc with major diffraction peaks of (1 0 0), (1 0 1), (1 0 2), and (1 1 0) planes (ICDD: 00-002-1280). There was another nickel sulfide phase ($\text{Ni}_{2.824}\text{S}$) present along with above phase and the peaks pattern of this phase are identified with “x”. The diffractions of cubic $\text{Ni}_{2.824}\text{S}$ in space group F-43m (2 1 6) with major diffraction peaks of (1 1 1), (2 2 0), and (3 1 1) planes (ICDD: 00-027-0343). The TEM image (Figure 3(c)) shows the particles are in spherical and irregular shapes having approximated 40–170-nm length.

4. Concluding remarks

- (1) We have successfully synthesized symmetrical and unsymmetrical nickel(II) complexes [*cis*-(C_3H_7)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Ni(II), [*cis*-(C_4H_9)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Ni(II), and [*cis*-(Hex)(Me)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Ni(II).
- (2) These newly synthesized metal complexes were used as single-source precursors for the deposition of nickel sulfide nanocrystals.
- (3) TEM images showed that the irregular-shaped nanocrystals deposited from precursors were in the range of 20–170-nm in length. These metal sulfide nanocrystals may be applied in photovoltaic devices, lithium ion batteries, and biological labeling.
- (4) These newly synthesized nickel complexes may also be useful as applicable precursors for the deposition of TOPO-capped (tri-*n*-octylphosphineoxide) nanocrystals of nickel sulfide.

Supplementary material

Supplementary material for this article can be accessed here <http://dx.doi.org/10.1080/23312009.2015.1030195>.

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