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Synthesis of Iron Sulfide Thin Films and Powders from New Xanthate Precursors

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Abstract

A series of novel alkylxanthato iron(III) precursors $[\text{Fe}(\text{S}_2\text{COR})_3]$ ($\text{R} = \text{n-butyl}$, (**1**); 2-butyl, (**2**); 2-methoxyethyl, (**3**); and 2-ethoxyethyl (**4**)) have been synthesised and their single crystal X-ray structures have been studied. All as-synthesised complexes were used as single-source precursors for the deposition of iron sulfide thin films as well as nanostructures using spin coating technique and solventless thermolysis respectively. Cubic pyrite was obtained using n-butyl xanthato iron(III) and 2-butyl xanthato iron(III) complexes in the temperature range of 200 to 300°C. Structural and morphological investigations using XRD and SEM have been performed to ascertain the crystallinity and morphology of as-prepared thin films and nanostructures. The elemental composition was determined using energy dispersive X-ray (EDX) spectroscopy. The optical band gaps of pyrite thin films produced by these methods were direct with estimated values in the range 1.6 to 2.3 eV.

Introduction

Semiconducting metal sulfides have excellent properties for optical, optoelectronic and electronic devices that have scientific and technological importance.¹⁻⁴ Among the various iron chalcogenides, the iron sulfides (Fe_xS_y) could be useful for sustainable energy applications as the constituent elements are abundant in the earth's crust and are mainly nontoxic.⁵ Iron

sulfide has a variety of crystalline phases, which includes cubic pyrite (FeS_2), orthorhombic marcasite (FeS_2), pyrrhotite (Fe_{1-x}S), cubic spinel greigite (Fe_3S_4), smythite (Fe_3S_4), troilite (FeS) and mackinawite (Fe_{1+x}S).⁶⁻¹⁰ Of these phases, pyrite is considered to be an important transition metal sulfide due to its semiconducting properties, high light absorption across the visible range ($\sim 5 \times 10^5 \text{ cm}^{-1}$) and its band gap energy of 0.95 eV.¹¹⁻¹⁴ This material has been researched for a range of applications such as commercial lithium ion cells, solar cells and for catalysis.¹⁵⁻¹⁸ Furthermore, it has also been used in optoelectronic devices, storage devices, energy conversion and biomedical applications.^{19,20} Nanostructured pyrite has been produced with control of morphology, phases and size which are strongly influenced by reaction parameters such as precursor type, deposition temperature and synthesis method. Several approaches have been used for the deposition of iron sulfide thin films such as chemical spray pyrolysis, aerosol assisted chemical vapor deposition (AACVD), metal organic chemical vapor deposition (MOCVD) and low-pressure chemical vapor deposition (LPCVD).²¹⁻²⁷ Furthermore, a wide range of single source precursors (SSPs) including dithiocarbamates, xanthates, thiosemicarbazone, thiobiuret and dithiobiuret have also been used for the deposition of iron sulfide thin films as well as to produce nanostructured materials.²⁸⁻³⁰ In addition, several methods have been utilized to synthesised iron sulfide nanostructures, such as hot injection method, solvothermal, hydrothermal and plasma assisted sulfurisation.³¹⁻³⁶ Recently, we have reported the use of iron alkyl xanthate with short carbon chain lengths as SSPs for the preparation of thin films and nanocrystalline materials.³⁷ These xanthate complexes produce the iron sulfides troilite (FeS) and pyrrhotite (Fe_{1-x}S).

Herein, we report a direct route to high quality iron sulfide thin films and nanostructures of various morphologies at low temperatures from molecular precursor chemistry. The single crystal X-ray structures of all as-synthesised complexes are also reported. We focus on studying three main factors which may affect materials growth, deposition method, temperature and precursor type in order to exert control over the structural, phase purities, size and morphology of the produced iron sulfide thin films and nanomaterials.

Experimental section

Chemicals and Instrumentation

All chemicals were purchased from Sigma-Aldrich and used as received without further purification. Infrared spectra (IR) were recorded using a Specac single reflectance ATR instrument (in the range $4000\text{-}400 \text{ cm}^{-1}$, resolution 4 cm^{-1}). Melting points were recorded

using a Barloworld SMP10 apparatus. Nuclear magnetic resonance (NMR) was obtained using a 400 MHz Bruker instrument. Elemental analysis (EA) was performed by The University of Manchester micro-analytical laboratory. Thermogravimetric analysis (TGA) measurements were carried out by a Seiko SSC/S200 model under a heating rate of 10 °C min⁻¹ under nitrogen. Thin films were deposited on glass substrates using spin coating (Ossila, 24 V DC, 2.01 A). X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance and a Bruker Xpert diffractometer with a Cu-K α radiation ($\lambda \sim 1.5406\text{\AA}$) with a step size of 0.02°. Scanning electronic microscopy (SEM) images were collected using a Philips XL30 FEG SEM. Films thickness was measured by stylus profilometry using a Bruker DektakXT system. UV-vis spectra were recorded using a Shimadzu UV-1800. Single crystal X-ray diffraction data for complexes were obtained using a dual source Rigaku FR-X rotating anode diffractometer, using MoK α wavelength at 150 K and reduced using a CrysAlisPro 171.39.30c. The structures were refined using Shelx-2016, implemented through Olex2 v1.2.9.³⁸⁻⁴⁰

Synthesis of Potassium n-Butylxanthate

The ligand was synthesised by the method described in literature.⁴¹ Briefly, carbon disulfide (CS₂) (6.78 g, 5.38 ml, 89.12 mmol) was added dropwise to a mixture of potassium hydroxide (5 g, 89.12 mmol) in n-butanol (60 mL) with stirring for 30 min. A yellow precipitate was then collected and purified by recrystallization in acetone to give [K(S₂COⁿBu)]. Yield 16.0 g (96%). Mp: 116–119°C. Anal. calc. for C₅H₉KOS₂ (%): C 31.90, H 4.82, S 33.99, K 20.78; found: C 31.72, H 4.65, S 33.45, K 21.66. FT-IR (ν_{max} /cm⁻¹): 2958 (m), 2942(w), 2869 (w), 1460 (m), 1444 (w), 1260 (s), 1148 (m), 1172 (m), 1053 (m), 1014(m), 747 (m), 669 (s). ¹H NMR (400 MHz, D₂O): δ ppm 0.89 (t, 3H, CH₃), 1.43 (m, 2H, CH₂), 1.67(m, 2H, CH₂), 4.43 (t, 2H, CH₂).

Synthesis of Potassium 2-Butylxanthate

[K(S₂CO²Bu)] was synthesized in a same way as potassium n-butylxanthate except replacing n-butanol with 2-butanol. The yield was (16.3 g 97.6 %), Mp: 110–123 °C. Anal. calc. for C₅H₉KOS₂ (%): C 31.90, H 4.82, S 33.99, K 20.78; found: C 31.72, H 4.65, S 33.45, K 21.66. FT-IR (ν_{max} /cm⁻¹): 2966 (m), 2929 (w), 2871(w), 1460 (m), 1455 (m), 1376 (m), 1178 (m), 1140(m), 1110 (s). ¹H NMR (400 MHz, D₂O): δ ppm 0.85 (t, 3H, CH₃), 1.23 (d, 3H, CH₃), 1.60 (m, 2H, CH₂), 5.33 (m, H, CH).

Synthesis of Potassium 2-Methoxyethylxanthate

[KS₂CO-(CH₂)₂OMe] was synthesized according to the reported literature.^{42,43} In typical reaction, KOH (5 g, 89.12 mmol) was dissolved in a mixture of 2-methoxyethanol (50 ml) and distilled water (20 ml) at room temperature. A drop-wise addition of CS₂ (6.78 g, 5.38 ml, 89.12 mmol) into KOH solution was performed with stirring. A yellow precipitate rapidly formed which then collected by vacuum filtration and washed several times with petroleum ether. The crude product was recrystallized from 2-methoxyethanol. Yield 16.2 g (96%), Mp: 201–204 °C. Anal. calc. for C₄H₇KO₂S₂ (%): C 25.25, H 3.71, S 33.69, K 20.57; found: C 25.48, H 3.67, S 33.51, K 20.93. FT-IR (ν_{max}/cm⁻¹): 2970 (m), 2937 (w), 2883(w), 1673(s), 1455 (m), 1592 (s), 1295 (s), 1210(s), 997 (s). ¹H NMR (400 MHz, D₂O) δ (ppm) =3.37 (s, 3H, OCH₃), 3.75 (t, 2H, CH₂CH₂O), 4.50 (t, 2H, CH₂CH₂O).

Synthesis of Potassium 2-Ethoxyethylxanthate

[K(S₂CO-(CH₂)₂OEt)] was synthesized in a same way as potassium n-butylxanthate except replacing 2-methoxyethanol with 2-ethoxyethanol. Yield 17.6 g (97 %), Mp: 160–180 °C. Anal. calc. for C₅H₉KO₂S₂ (%): C 29.40, H 4.44, S 31.33, K 19.16; found: C 29.27, H 4.37, S 30.86, K 19.64. FT-IR (cm⁻¹): 2972 (w), 2859 (w), 1443(m), 1421(w), 1290 (w), 1246 (w), 1107(m), 1053 (s), 934 (w), 826 (w), 795 (w). ¹H NMR (400 MHz, D₂O) δ (ppm) =1.17 (t, 3H, CH₃), 3.60 (m, 2H, CH₂), 3.80 (t, 2H, CH₂CH₂O), 4.53 (t, 2H, CH₂CH₂O).

Synthesis of Iron (III) n-Butyl xanthate (1)

The complex was synthesized according to the reported literature.⁴¹ Briefly, an aqueous solution of iron (III) chloride (FeCl₃) (1.4 g, 8.8 mmol, 1.0 eq.) was added dropwise into an aqueous solution potassium n-butyl xanthate (5 g, 26.5 mmol, 3.0 eq.) with stirring continued for 30 min post-addition. The black crude product was collected by suction filtration and washed with distilled water. Shiny black crystals of the title product were recrystallized from chloroform at -20 °C. Yield 3.5 g (80%). Mp: 70-79 °C. Anal. calc. for C₁₅H₂₇FeO₃S₆ (%): Calc. C 35.79, H 5.41, S 38.15, Fe 11.11; found: C 35.46, H 5.33, S 37.39, Fe 10.99. FT-IR (cm⁻¹): 2957 (m), 2920 (w), 2871(w), 1744(w), 1460 (m), 1384 (m), 1250 (s), 1207 (s), 1141 (m), 1115 (s), 1010 (s).

Synthesis of Iron (III) 2-Butyl xanthate (2)

A similar method was used for the synthesis of [Fe(S₂CO₂Bu)₃] using 3.0 eq. of potassium 2-butylxanthate. The crude product was recrystallized from chloroform at -20 °C. Yield 4.1

g (94%). Mp: 82-90 ° C Anal. calc. for $C_{15}H_{27}FeO_3S_6$ (%): Calc C 35.79, H 5.41, S 38.15, Fe 11.11; found: C 35.93, H 5.41, S 38.14, Fe 11.14. FT-IR (cm^{-1}): 2970 (s), 2933 (m), 2875 (w), 1455 (m), 1377 (m), 1240 (s), 1120 (m).

Synthesis of Iron (III) 2-Methoxyethylxanthate (3)

The synthesis of $[Fe(S_2CO(CH_2)_2OMe)_3]$ was done according to complex (1), using the potassium 2-methoxyethylxanthate. Yield 4.0g (91%). Mp: 140-158 °C. Anal. calc. for $C_{12}H_{21}FeO_6S_6$ (%): Calc C 28.30, H 4.16, S 37.70, Fe 10.98; found: C 28.51, H 54.22, S 37.35, Fe 10.72. FT-IR (v_{max}/cm^{-1}): 2983 (m), 2886 (w), 2817(w), 1745 (w), 14552 (m), 1367 (s), 1254 (s), 1124 (m).

Synthesis of Iron (III) 2-Ethoxyethylxanthate (4)

The synthesis of $[Fe(S_2CO(CH_2)_2OEt)_3]$ was done according to complex (1), using the potassium 2-ethoxyethylxanthate. Yield 3.6 g (80%). Mp: 127-130 ° C. Anal. calc. for $C_{15}H_{27}FeO_6S_6$ (%):C 32.68, H 4.94, S 34.82, Fe 10.14; found: C 32.66, H 4.94, S 33.26, Fe 9.84. FT-IR (cm^{-1}): 2972 (m), 2872 (m), 1448 (m), 1384 (m), 1353 (m), 1239 (s), 1036 (s).

Preparation of iron sulfide thin films and powders

Iron sulfide thin films were deposited on glass substrates. The glass substrates were cleaned ultrasonically in isopropanol, distilled water and finally with acetone and allowed to dry prior to use. The deposition was done using spin coating technique. In a typical deposition process, 0.13 g of precursor was dissolved in 0.5 ml of chloroform to form clear solution, which was dropped on glass substrate at room temperature and rotated at 1400 rpm for 30 sec to make thin films of the precursor. The films were annealed in tube furnace at different temperatures (200 - 300 °C) under nitrogen atmosphere for an hour to produce iron sulfide thin films.

The iron sulfide powders were synthesized using solventless thermolysis (melt method). Briefly, 0.4 g of solid precursor was placed in a ceramic boat in a tube furnace and then heated at the desired temperatures (200 - 300 °C) in an inert atmosphere (N_2) for an hour.

Results and discussion

Thermogravimetric analysis (TGA)

Thermal decomposition of iron(III) xanthates complexes (1) – (4) were evaluated by thermogravimetric analysis (TGA) as shown in Figure 1. The precursors were heated from

50 to 600 °C under nitrogen atmosphere. Complexes **(1)** and **(2)** decomposed in two steps with a rapid weight loss between 120 to 200 °C. The solid decomposition residue amounts to 22 and 20 %, respectively, which is commensurate with decomposition to FeS₂ (theoretically *ca.* 23%). A gradual decomposition between 200 to 300 °C is then observed for both complexes with weights of final residues of 19% and 19% of the original mass which is in good agreement with calculated values for FeS 19% and 19%, respectively for **(1)** and **(2)**. Similar thermal decomposition behaviour was observed for complex **(3)** with final residue amount of 24%, which corresponds to FeS (theoretically *ca.* 24%). In contrast, complex **(4)** shows slightly different decomposition behaviour, it shows multi-step decomposition with a final residue amount of 22 %, which is in agreement with the calculated value of 21% for FeS₂.

Figure 1. Thermogravimetric analysis (TGA) of complexes [Fe(S₂COⁿBu)₃], **(1)**, [Fe(S₂CO²Bu)₃] **(2)**, [Fe(S₂CO-(CH₂)₂OMe)₃] **(3)** and [Fe(S₂CO-(CH₂)₂OEt)₃] **(4)**.

Single-crystal X-ray structures of Fe complexes

All four complexes adopt distorted octahedral coordination arrangement around the centre of iron ion with a six sulfur (S₆) donor set. Each iron ion is chelated by three bidentate xanthate ligands (Figure 2). The complexes **(1)**, **(2)** and **(3)** were crystallized in the monoclinic system with space group of *P* 21/n, *P* 21 and *p* 21/n, respectively. Whereas, the complex **(4)**

crystallized in the triclinic system with a space group of P-1. The structural refinement data, selected bond lengths and angles are summarized in the ESI Table (S1- S6). Relatively little variation was observed in the Fe-S bond length across the series, which are in the range 2.295(1) -2.322(1) Å (**1**), 2.284 (2) -2.314(2) Å (**2**), 2.305(6) -2.323(6) Å (**3**) and 2.299 (1) - 2.305(1) Å (**4**) for each of the complexes.

Figure 2. X-ray single crystal structures of complexes (**1**), (**2**), (**3**) and (**4**). Yellow spheres = sulfur, orange spheres = iron, red spheres = oxygen, grey spheres = carbon.

Iron sulfide thin films

Iron disulfide (FeS_2) thin films were prepared using low-cost spin-coating method. We have chosen this method because it is unique and efficient to deposit thin films by simple and low fabrication costs route with control over thickness. Pyrite (FeS_2) thin films were deposited on the substrates using chloroform solution of iron alkyl xanthate precursor (**1**) - (**4**).

According to TGA results, the complexes decompose completely between 180 °C to 190 °C. So the annealing temperatures were varied between 200 and 300 °C. The films were prepared by coating glass slides with the precursor solution, followed by annealing at three different

temperatures of 200, 250 and 300 °C for 1 h in order to study the effect of growth temperatures on obtained materials. The resulting films were uniform black thin films at all the growth temperatures. The thickness measurement of pyrite films from complex (1) deposited at 200, 250 and 300 °C was 337, 355 and 370 μm respectively (ESI Table S7).

The phase purity and crystal structures of iron sulfide thin films were identified using powder X-ray diffraction (p-XRD). The p-XRD pattern of iron disulfide thin films prepared using a spin coated chloroform solution of complexes (1) and (2) are presented in (Figure 3 and ESI Figure S1). The XRD patterns, showed the formation of phase-pure FeS₂ thin films at all annealing temperatures between 200 to 300 °C with no additional peaks of any impurities or other phases. The two major peaks at $2\theta = 28.58^\circ$ and 58.86° are assigned to the (111) and (222) reflections of cubic pyrite (FeS₂) ICDD 01-089-3057) (ESI Figure S3). Growth temperature does not affect the phase of iron disulfide for complexes (1) and (2), suggesting that pyrite is a kinetic product from the decomposition of these precursors. This is in contrast to previous studies with short chain xanthates that produced troilite and pyrrhotite and allows access to new phases by judicious precursor choice.

The p-XRD pattern of iron sulfide thin films prepared using complexes (3) and (4) are shown in (Figure 4 and ESI Figure S5). The major diffraction peaks with reflections of (111), (211), (221) and (222) corresponds to cubic pyrite while a minor peak at 66.4° corresponds to orthorhombic marcasite phase (FeS₂) (ICDD. No. 00-003-0799). It is clear from the p-XRD patterns of films deposited from precursors (1) and (2) that thin films show only two peaks which indicated that the preferred orientation along the (111) and (222) planes under all the deposition conditions. Also, the thin films growth from precursors (3) and (4) show variation on peaks intensity comparing with the standard pattern which indicates to the preference orientation for the obtained crystallites. This behaviour of crystallite that has preferred orientation have been noticed with lead sulfide (PbS) thin films deposited by AACVD method.⁴⁴ This suggests that the substrate under these conditions exerts control over the nucleation and growth of iron sulfide thin films. The p-XRD shows sharp and narrow peaks which attributed to high crystallinity of the thin films.

Commonly, the formation of pyrite is potentially accompanied by marcasite impurities,⁴⁵ and indeed these are observed when complexes (3) and (4) were used as precursors to deposit thin films. However, the purity of pyrite could be controlled by selection of precursor type which has influence on purity of pyrite phase as shown in results obtained from thin films deposited using complex (1) and (2), which show a pure pyrite phase.

The micro and nanoscale morphology of iron sulfide thin films were studied by scanning electron microscopy (SEM). Micrographs of FeS₂ thin films deposited by spin coating method from complexes **(1)** and **(2)** at growth temperatures of 200, 250 and 300 °C are shown in Figure 5(1a-1d) and ESI Figure S7. Cubic crystallites with an average size range between 38 nm to 180 nm (size increasing with temperature) were observed in all samples produced from thermal decomposition of complexes **(1)** and **(2)**. Small crystallites with no defined morphology were obtained at all deposition temperatures for pyrite thin films prepared using precursor **(3)** as shown in Figure 5 (2a, 2b) and ESI Figure S8. Semi-cubic crystallites were obtained at all deposition temperatures when complex **(4)** is used as precursor (Fig. 5 (2c-2d)) and ESI Figure S5.

Elemental analysis using EDX spectroscopy of the films prepared using complexes **(1)** to **(4)** agreed well with the expected 1:2 Fe: S stoichiometry of pyrite (ESI Table S8). Variation in the morphological properties of the resulting films suggests that the type of precursors used in deposited thin films have an important role on controlling microstructure, which can be seen in Figure 5.

Figure 3. Powder X-ray diffraction (PXRD) patterns of the iron sulfide thin films obtained by spin coating using [Fe(S₂CO^tBu)₃] **(1)** and [Fe(S₂CO²Bu)₃] **(2)**, followed by annealing under nitrogen at 250°C (a) and 300°C (b) for 60 min.

Figure 4. PXRD patterns of the iron sulfide thin films obtained by spin coating $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OMe})_3]$ **(3)** and $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OEt})_3]$ **(4)**, followed by annealing under nitrogen at 250°C (a) and 300°C (b) for 60 min. The asterisk symbols (*) correspond to reflections from orthorhombic marcasite (ICDD: 00-003-0799).

Figure 5. SEM images of iron sulfide thin films by spin coating method from $[\text{Fe}(\text{S}_2\text{CO}^i\text{Bu})_3]$ (1a) at 250°C and (1b) at 300 °C, $[\text{Fe}(\text{S}_2\text{CO}^i\text{Bu})_3]$ (1c) at 250°C and (1d) at 300 °C, $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OMe})_3]$ (2a) at 250°C and (2b) at 300 °C, and $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OEt})_3]$ (2c) at 250°C and (2d) at 300 °C.

Figure 6. Powder X-ray diffraction (p-XRD) patterns of the iron sulfide nanostructure obtained by solventless thermolysis method using $[\text{Fe}(\text{S}_2\text{CO}^t\text{Bu})_3]$, **(1)** and $[\text{Fe}(\text{S}_2\text{CO}^2t\text{Bu})_3]$ **(2)**, annealing under nitrogen at 250 °C (a) and 300 °C (b) for 60 min. The asterisk symbols (*) correspond to reflections from cubic pyrite (ICDD: 01-089-3057).

Iron sulfide nanostructures

This work includes preparation of iron sulfide nanostructures in the absence of any solvent. Thermolysis is a low-cost and simple route toward the development of semiconductor materials. Commonly, this method produces high yields in comparison with other method such as hot injection.

All the complexes were used as single molecular precursors to synthesise iron sulfide thin films as well as **nanostructures** using spin coating technique and solventless thermolysis method. The p-XRD patterns of iron sulfide nanomaterial prepared using complexes **(1)** and **(2)** show the formation of phase-separated pyrrhotite (ICDD: 01-075-0600) (ESI Figure S5) and cubic pyrite at all growth temperatures (Figure 6 and ESI Figure S4). The (100), (101), (102) and (110) reflections of hexagonal pyrrhotite are superimposed on the diffraction pattern of cubic pyrite (FeS_2). These data also show that by increasing the synthesis temperature to 300 °C, the pyrrhotite phase becomes dominant, which suggests that in this case, the choice of phase could be dictated by judicious choice of reaction temperature. The p-XRD patterns for iron sulfide powders obtained using complexes **(3)** and **(4)** are shown in Figure 5 and ESI Figure S6. The presence of phase separated cubic greigite and cubic pyrite

phases are observed at all growth temperatures. The major diffraction peaks of (111), (211), (221) and (222) plans correspond to cubic pyrite phase (ICCD No. 01-089-3057).

Figure 7. PXRD patterns of the iron sulfide powders obtained by thermolysis method of $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OMe})_3]$ (**3**) and $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OEt})_3]$ (**4**), under nitrogen at 250°C (a) and 300°C (b) for 60 min. The asterisk symbol (*) represent cubic Greigite (ICDD: 00-016-0713).

SEM images of iron sulfide nanostructure powders produced using complexes (**1**) and (**2**) as precursors comprised of pseudo spherical like crystallites (Figure 8 (1a-1f)). Flower-like crystallites are observed from powders produced from (**3**) at temperatures in the range of 200 – 300 °C (Figure 8 (2a, -2c)). In contrast, iron sulfide powders produced from complex (**4**) have no obvious morphology at the resolution offered by SEM (Figure 8 (2d-2f)). No significant changes in morphologies were noticed when the growth temperature was increased. Elemental analysis of nanostructure powder samples of complexes (1) to (4) using EDX spectroscopy were summarised in ESI Table S9.

The obtained structural and morphological results from all precursors using two different routes were summarised in Table 1. There is a massive difference between the results obtained using spin coating and melt thermolysis routes. The p-XRD results obtained from spin coating method result in formation of pyrite with preferred orientation, whereas the mixed phase with randomly oriented nanocrystals?? were observed when thermolysis method is used. Importantly, the approaches demonstrated in this work provide simple, low-cost and

promising methods to synthesise a variety of nanomaterials?? with different size and morphology.

Figure 8. SEM images of iron sulfide powders produced by solventless thermolysis from $[\text{Fe}(\text{S}_2\text{CO}^i\text{Bu})_3]$ (1a) at 200 °C (1b) at 250 °C and (1c) at 300 °C, $[\text{Fe}(\text{S}_2\text{CO}^2\text{Bu})_3]$ (1d) at 200 °C, (1e) at 250 °C and (1f) at 300 °C, $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OMe})_3]$ (2a) at 200 °C (2b) at 250 °C and (2c) at 300 °C, and $[\text{Fe}(\text{S}_2\text{CO}-(\text{CH}_2)_2\text{OEt})_3]$ (1d) at 200 °C, (1e) at 250 °C and (1f) at 300 °C.

Precursor	growth temperature °C	Phase and Morphology obtained by spin coating method	Phase and Morphology obtained by thermolysis method
(1)	200, 250 and 300	Pyrite ,cubic	Hexagonal pyrrhotite and Pyrite , pseudo spherical like crystallites
(2)	200, 250 and 300	Pyrite ,cubic	Hexagonal pyrrhotite and Pyrite, pseudo spherical like crystallites
(3)	200, 250 and 300	Pyrite and marcasite, Small crystallites with no defined morphology	Pyrite and greigite, Flower-like crystallites
(4)	200, 250 and 300	Pyrite and marcasite, Semi-cubic	Pyrite and greigite, crystallites with no obvious morphology

Table 1. Summary of iron sulfide thin films and nanomaterials obtained from precursors **(1)** to **(4)** under different reaction conditions.

Optical properties of iron disulfide thin films

Figure 9 present the room temperature Ultraviolet–visible-Near Infrared (UV–Vis-NIR) absorption spectra of iron sulfide thin films deposited on glass substrate at three different temperatures (200, 250 and 300 °C) for 60 min using a complex (1). These pyrite thin films display light absorbance ranging from the far-UV to near infrared regions of the electromagnetic spectrum. The energy of the direct band gap was estimated from Tauc plots (a plot of $(\alpha h\nu)^2$ versus $h\nu$)⁴⁶ with a straight line fitting, with energies of 2.3, 1.9 and 1.6 eV extrapolated at deposition temperatures of 200, 250 and 300 °C respectively. It is clear from the spectra that the evaluated band gap of as-deposited pyrite thin films were significantly influenced by growth temperature, which demonstrates control of optical properties by changing the growth temperature.

Figure 9. UV-Vis-NIR absorption spectra and band gap plot of pyrite (FeS_2) thin films deposited from complex **(1)** on glass substrate at (a) 200, (b) 250 and (c) 300 °C.

These results are consistent with the previously reported literature for pyrite (FeS_2).^{48,49} Several reports have been investigated the pyrite band gap at different growth temperatures as represented in Figure 10. For example, a hydrothermal method was used to synthesise pyrite at growth temperature of 120 °C and the estimated direct band gap was 2.75 eV.⁵⁰ While a direct band gap of 1.22 eV was observed in pyrite produced using spray pyrolysis at a temperature of 350 °C.⁵¹ Dip and spin coating method were used to deposit pyrite at 220 and 450 °C the evaluated band gap was direct with band energy values of 1.38 and 1.24 eV respectively.^{52,53} The variation in the band gap among these studies could be attributed to many factors such as microstrain as well as particle size effects.

Figure 10. Pyrite band gaps obtained at different growth temperatures. The red data points represent band gap energies reported in literature whereas the data in blue represents the band gap energies reported in this work.

Conclusions

Novel iron alkyl xanthate complexes have been successfully synthesized and their single crystal X-ray structures elucidated. The as-synthesized complexes were used as single source precursors to deposit iron sulfide thin films and powders at different growth temperatures in the range of 200 to 300 °C. The effect of precursor type and deposition temperatures on the structure and morphology of the products have been investigated in details. In general, pure phase of cubic disulfide (pyrite) was deposited from complex (1) and (2) using spin coating technique. Whereas the mixed phases of cubic pyrite (FeS_2) and hexagonal pyrrhotite (Fe_{1-x}S) nanostructure were obtained using melt thermolysis approach. In case of complexes (3) and (4), the mixed phases of cubic pyrite and cubic greigite were observed for nanostructure prepared using thermolysis method, whereas a cubic pyrite phase with minor impurities of hexagonal pyrrhotite was obtained for the film prepared using spin coating technique. This leads to two important conclusions. Firstly, the products from spin coating-annealing are generally phase pure materials where the product phase is independent of the precursor used, suggesting that the spin coating technique imposes some kinetic limitation on the growth of other phases in the thin film. Secondly, that solventless thermolysis largely gives different products to spin-coating annealing, in this case phase-separated iron sulfides (e.g. pyrite + greigite), and that synthesis temperature plays a much larger role in the choice of phase

produced, which may suggest that different reaction pathways are introduced by reaction within a melt as compared to decomposition of thin films of precursors.

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