Single-molecule precursor-based approaches to cobalt sulphide nanostructures

BY KARTHIK RAMASAMY, WEERAKANYA MANEERPRAKORN, MOHAMMAD A. MALIK AND PAUL O’BRIEN*

School of Chemistry and Manchester Material Science Centre, University of Manchester, Oxford Road, Manchester M13 9PL, UK

Cobalt complexes of 1,1,5,5-tetramethyl-2,4-dithiobiuret, [Co{N(SCNMe₂)₂}₂] (1), and 1,1,5,5-tetraisopropyl-2-thiobiuret, [Co{N(SOCNiPr₂)₂}] (2), have been synthesized and characterized. Both complexes were used as single-molecule precursors for the preparation of cobalt sulphide nanoparticles by thermolysis in hexadecylamine, octadecylamine or oleylamine. The powder X-ray diffraction pattern of as-prepared nanoparticles showed the hexagonal phase of Co₁−ₓS from complex 1 and mixtures of cubic and hexagonal Co₄S₃ from complex 2. Transmission electron microscopy images of material prepared from complex 1 showed spherical and trigonally shaped particles in the size range of 10–15 nm; whereas spheres, rods, trigonal prisms and pentagonally and hexagonally faceted crystallites were observed from complex 2. This observation is the first of the Co₄S₃ phase in a nanodispersed form.

Keywords: single-source precursor; thiobiuret; dithiobiuret; cobalt sulphide; nanoparticles

1. Introduction

Cobalt sulphides form a group of II–IV semiconductor materials with considerable potential for application in electronic devices. They can be used in solar energy as absorbers (Smith et al. 1980), ultra-high-density magnetic recording (Whitney et al. 1993), anodes for Li-ion batteries (Yue et al. 2007) and catalysts for hydrodesulphurization and dehydrodearomatization (Feng et al. 2008). It is also one of the more complicated metal sulphide systems, with a number of phases and differing chemical compositions, including Co₄S₃, Co₉S₈, CoS, Co₁−ₓS, Co₅S₄, Co₂S₃ and CoS₂ (Rao & Pisharody 1976; Chen et al. 2007). The diversity in the stoichiometry of cobalt sulphides poses a challenge for the control of size and shape in small-particle synthesis, which is exacerbated by the potential coexistence of the strongly reducible cobalt ion and oxidizable sulphide ion (Bao et al. 2008). There have been many efforts directed towards the deposition of cobalt sulphide thin films by methods such as chemical bath deposition (CBD) (Yu et al. 2002), chemical vapour deposition (CVD) (Ge & Li 2003; Srouji et al. 2005), electrochemical

*Author for correspondence (paul.obrien@manchester.ac.uk).

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deposition (ECD) (Yue et al. 2007) and Langmuir–Blodgett (LB) (Luo et al. 1994). Nanoparticles of cobalt sulphide have been synthesized by hydrothermal (Liu 2005) or solvothermal methods (Qian et al. 2000), microwave-assisted techniques (Chen et al. 2003) and the thermolysis of single-source precursors (Dutta et al. 2008; Maneerprakorn et al. 2010). In our continuing search for routes to semiconductor nanoparticles from single-source precursors (Trindade et al. 2001; Pickett & O’Brien 2001; Li et al. 2006; Fan et al. 2007; Afzaal et al. 2010), we now report the synthesis of cobalt complexes of 1,1,5,5-tetramethyl-2,4-dithiobiuret, [Co{N(SCNMe2)2}3] (1), and 1,1,5,5-tetraisopropyl-2-thiobiuret, [Co{N(SOCNiPr2)2}2] (2), and their use for the selective synthesis of Co1−xS and Co4S3 phase cobalt sulphide nanoparticles.

2. Experimental

All preparations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All reagents were purchased from Sigma-Aldrich and used as received. Solvents were distilled prior to use. Mass spectra were recorded on a Kratos Concept 1S instrument. Infrared (IR) spectra were recorded on a Specac Single Reflectance ATR instrument (4000–400 cm−1, resolution 4 cm−1). Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Thermogravimetric analysis measurements were carried out by a Seiko SSC/S200 model at a heating rate of 10°C min−1 under nitrogen.

\( a \) Synthesis of [Co{N(SCNMe2)2}3] (1)

A solution of dimethylthiocarbamyl chloride (1.23 g, 10 mmol) and sodium thiocyanate (0.81 g, 10 mmol) in acetonitrile (40 ml) was heated under reflux with continuous stirring for 1 h, during which time a fine precipitate of sodium chloride was formed. To the cooled reaction mixture, 60 per cent aqueous dimethylamine was added (1.49 ml, 20 mmol), followed by stirring for 30 min and the addition of cobalt acetate hexahydrate (1.19 g, 5 mmol). The crude product was precipitated as a red powder and recrystallized from chloroform followed by tetrahydrofuran. Yield was 1.89 g (30%). Mass spectrometry (atmospheric-pressure chemical ionization) (MS (APCI)) major fragments: \( m/z = [M^+] \) 631, [Co{N(SCNMe2)2}3] 631, [N(SCNMe2)2] 190. IR (\( \nu_{\text{max}}/\text{cm}^{-1} \)) - 2928(w), 1468(s), 1380(m), 1306(s), 1104(s), 906(s). Elemental analysis: Calculated for C18H36N9S6Co: C, 34.1; H, 6.1; N, 19.9; S, 30.3; Co, 9.3%. Found: C, 34.9; H, 6.0; N, 19.7; S, 28.9; Co, 9.1%.

\( b \) Synthesis of [Co{N(SOCNiPr2)2}2] (2)

A solution of diisopropylcarbamyl chloride (1.0 g, 6 mmol) and sodium thiocyanate (0.49 g, 6 mmol) in acetonitrile (25 ml) was heated under reflux with continuous stirring for 1 h, during which time a fine precipitate of sodium chloride formed. To the cooled reaction mixture, diisopropylamine (1.49 ml, 12 mmol) was added, followed by stirring for 30 min and addition of cobalt acetate tetrahydrate (0.76 g, 3 mmol). The crude product was precipitated as blue powder and recrystallized from tetrahydrofuran to get shiny crystals of blue needles, which

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were identified as 2. Yield was 1.89 g (30%). Melting point: 176°C. MS (APCI) major fragments: \( m/z = [M^+] \) 631, \([\text{Co(C}_{14}\text{H}_{28}\text{N}_3\text{OS})_2] \), \([\text{NSO(CNiPr}_2)_2] \) 284. IR \( (v_{\text{max}} \text{ cm}^{-1}) \): 2963(s), 1499(s), 1434(s), 1353(s), 1208(m), 1144(m). Elemental analysis: Calculated for \( \text{C}_{28}\text{H}_{56}\text{N}_6\text{S}_2\text{O}_2\text{Co} \): C, 53.2; H, 8.8; N, 13.3; S, 10.1; Co, 9.3%. Found: C, 53.2; H, 9.0; N, 13.2; S, 9.9; Co, 9.0%.

(c) Preparation of cobalt sulphide nanoparticles

In a typical experiment, hexadecylamine (HDA) (10 g) was degassed under reduced pressure at 50°C and then heated to 230°C under nitrogen. The cobalt precursor \([\text{Co(N(SCNMe}_2)_2)_3] \) or \([\text{Co(N(SOCNiPr}_2)_2)_2] \) (0.5 g) was dispersed in trioctylphosphine and injected into the hot solution. The reaction was maintained at 230°C for 1 h. The dark solution formed was cooled to approximately 70°C. After cooling the reaction mixture, an excess of methanol was added and the solid was isolated by centrifugation. The solid was washed several times with methanol and left to dry at room temperature. The procedure was repeated with octadecylamine (ODA) and oleylamine (OA) replacing HDA as the capping group.

(d) Characterization of nanoparticles

X-ray diffraction (XRD) studies were performed on a Bruker AXS D8 diffractometer using Cu Kα radiation. The samples were mounted flat and scanned between 20° and 80° in a step size of 0.05° with a count rate of 9 s. Transmission electron microscope (TEM) analysis was performed using cm120 BIOTWIW and Philips cm 200 microscopes. High-resolution transmission electron microscopy (HR-TEM) was performed using a JEOL 2100 TEM instrument, operating at 200 kV, and a Tecnai operating at 300 kV. All samples were deposited over carbon-coated copper grids. Selected-area electron diffraction (SAED) was performed using a cm120 BIOTWIW microscope at an accelerating voltage of 80 kV and a Philips cm 200 microscope.

3. Results and discussion

The symmetrical S,S- and S,O- bidentate ligands of 1,1,5,5-tetramethyl-2,4-dithiobiuret and 1,1,5,5-tetraisopropyl-2-thiobiuret were prepared by the reaction of dialkylcarbamyl chloride, sodium thiocyanate and dialkylamine (Ramasamy et al. 2010). The addition of cobalt acetate to this reaction gave the corresponding cobalt complexes. A molecular ion peak at 631 in the APCI mass spectrum confirms the formation of the complexes and peaks at 190 and 284 further confirm the presence of the ligands. The purity of the complex was further analysed by elemental analysis. A schematic of the synthetic methodology is shown in scheme 1. Thermogravimetric analysis of \([\text{Co(N(SCNMe}_2)_2)_3] \) (1) shows that the precursor decomposed in a single step between 228 and 320°C. The observed final residue of 20.0 per cent is in good agreement with the 19.5 per cent calculated for cobalt disulphide. Similarly complex \([\text{Co(N(SOCNiPr}_2)_2)_2] \) (2) also decomposed in a single step between 140 and 230°C with the final residue of 18.0 per cent close to the calculated value of 19.5 per cent for cobalt disulphide. The powder

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Figure 1. XRD patterns of (a) ODA-capped and (b) HDA-capped hexagonal Co$_{1-x}$S phase cobalt sulphide nanoparticles prepared at 230°C from [Co{N(SCNMe$_2$)$_2$}$_3$] (1) (JCPDS-042-0826).

X-ray diffraction (PXRD) of the final residue obtained from pyrolysis at 250°C under argon atmosphere indicates predominantly hexagonal Co$_{1-x}$S from complex 1 whereas complex 2 gave cubic Co$_4$S$_3$.

(a) Cobalt sulphide nanoparticles from [Co{N(SCNMe$_2$)$_2$}$_3$] (1)

Cobalt sulphide nanoparticles were synthesized by the thermal decomposition of complex 1 in hot surfactant solution. The nanoparticles prepared from 1 were hexagonal Co$_{1-x}$S with size and shape dependent upon the reaction time and capping agent. The crystalline nanoparticles were characterized by XRD and TEM. Figure 1 shows typical PXRD patterns of the ODA- and HDA-capped cobalt sulphide nanoparticles prepared at 230°C from 1. The patterns are well
Figure 2. (a–c) TEM images of HDA-capped cobalt sulphide nanoparticles prepared from complex 1 at 230°C after (a) 1h, (b) 3h and (c) 1h, at lower magnification. (d) SAED pattern and inset (b) HR-TEM image of same nanoparticles. (e–g) TEM images of ODA-capped cobalt sulphide nanoparticles prepared from complex 1 at 230°C after (e) 1h, (f) 3h and (g) 1h, at lower magnification. (h) HR-TEM image of same nanoparticles. Scale bars: (a,b,e,f) 50 nm, (c,g) 200 nm, (h) 5 nm; and inset (b) 5 nm.
defined, characterized by the (100), (101), (102) and (110) reflections of hexagonal Co$_{1-x}$S (Joint Committee on Powder Diffraction Standards–International Centre for Diffraction Data, no. JCPDS-042-0826). Energy-dispersive X-ray (EDX) analysis shows the composition of the nanoparticles as cobalt : sulphur = 49.5 : 50.5. There was a distinct change in particle shape as reaction conditions such as reaction time and capping group were varied. In HDA after 1 h of reaction monodispersed close-to-spherical Co$_{1-x}$S nanoparticles were seen; a few irregular-shaped particles were also seen in the TEM image (figure 2a). The average diameter of the particles was ca 10 ± 1 nm. When the reaction time was increased to 3 h, trigonally faceted particles with an average edge length of 15 ± 1 nm were seen (figure 2b).

Particles prepared using ODA at 230°C over 1 h (figure 2c) gave predominantly spherical particles with an average diameter of 8 ± 1.5 nm, whereas the particles obtained after 3 h (figure 2f) were spherical with a diameter of 10 ± 2 nm.

The HR-TEM image of the cobalt sulphide nanoparticles (figure 2h) shows lattice fringes with a d-spacing 0.254 nm corresponding to the (101) reflection of hexagonal Co$_{1-x}$S. The SAED patterns for these samples are shown in figure 2d. The patterns show the presence of distinct diffraction rings, confirming the polycrystalline nature of the particles, and the diffraction rings could be indexed to the (101), (102) and (110) planes of the Co$_{1-x}$S phase.

(b) Cobalt sulphide nanoparticles from [Co{N(SOCN$_3$Pr)$_2$}]$_2$ (2)

Cobalt sulphide nanoparticles were synthesized by the thermal decomposition of complex 2 in OA solution. The nanoparticles prepared from this precursor gave a mixture of hexagonal and cubic cobalt sulphides with different sizes and shapes depending upon the reaction temperature and the concentration of the capping agent.

The crystalline nanoparticles have been characterized by using XRD and TEM. Figure 3 shows the typical XRD pattern of the nanoparticles prepared at 250°C by using a precursor : OA ratio = 1 : 100. The pattern shows a
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Figure 4. TEM images of the mixed phase Co$_4$S$_3$ nanoparticles obtained from complex 2 at different reaction temperatures, reactant ratios and reaction times. (a–c) Reaction temperature of (a) 230°C, (b) 250°C and (c) 270°C (at precursor : OA = 1 : 50, precursor 0.5 g, OA 15 ml, and 30 min reaction time). (d–f) Precursor:OA ratio of (d) 1:50, (e) 1:100 and (f) 1:200 (at 250°C and 60 min reaction time). (g–i) Reaction time of (g) 10 min, (h) 20 min and (i) 30 min (at precursor:OA = 1:50 at 250°C). The insets in (a–c) are the corresponding SAED patterns. Scale bars: (a,b,h) 20 nm, (c,f) 50 nm, (d,e,i) 100 nm and (g) 10 nm.

mixture of hexagonal Co$_4$S$_3$ (JCPDS-02-1458) and face-centred cubic Co$_4$S$_3$ (JCPDS-02-1338) with well-defined characteristic (311), (222), (331) and (511) reflections of cubic Co$_4$S$_3$ and (100), (101), (102), (003), and (110) planes of hexagonal Co$_4$S$_3$ phase. EDX analysis shows the composition of the nanoparticles as cobalt : sulphur = 59.7 : 40.3.

The TEM of these nanoparticles showed monodispersed, close-to-spherical crystallites. However, there was a remarkable change in the shape of the nanoparticles with temperature and time. At 230°C (figure 4a), monodispersed close-to-spherical Co$_4$S$_3$ nanoparticles were observed with a small number of
irregularly shaped nanoparticles. These particles have an average diameter of 7.3 ± 1 nm. At 250°C, more spherical nanoparticles were observed with an average diameter of 11 ± 1.5 nm (figure 4b). At the highest temperature of 270°C, variously shaped nanoparticles including triangular prisms, trapezoids, rods, hexagons and spheres were obtained (figure 4c). The average diagonal for all morphologies increased to ca 16 nm. The SAED patterns for these samples are shown in the insets of figure 4a–c. The patterns show the presence of distinct diffraction rings, confirming the crystalline nature of the particles.

The factors controlling the shapes of inorganic nanocrystals involve competition between thermodynamic and kinetic factors (Lee et al. 2003; Christian & O’Brien 2008). According to this model, after the formation of a preferred crystalline phase seed, the final morphology of the nanocrystals is mainly determined by the growth process through a balance between kinetic growth and thermodynamic preference. At high temperature, the reaction is under thermodynamic control and the most stable form of nanocrystal is generally preferred. At lower temperature, the reaction may be under kinetic control and selective anisotropic growth may occur. In our system, the deposition at 230°C produced a mixture of spherical and irregular shapes of nanoparticles (figure 4a). When the temperature is increased to 250°C, the product is controlled by thermodynamics and the nanoparticles are predominantly spherical. The sphere can be considered as a preferred shape of minimized surface area under limiting thermodynamic control (Lee et al. 2003) (figure 4b). However, at the highest temperature of 270°C, the transformation of small nanoparticles into other particle geometries probably occurs via the Ostwald ripening process (An et al. 2007).

The effect of reactant concentration (precursor:OA molar ratio) on the formation of nanoparticles was investigated. Three different molar ratios of precursor to OA (1:50, 1:100 and 1:200) were studied. The concentration of the precursor has dramatic effects on both nanoparticle size and shape. TEM images of the Co₄S₃ nanoparticles at different molar ratios are shown in figure 4.

At 1:50 precursor:OA ratio, the mixed shapes of triangular, hexagonal and rod nanoparticles were observed, with a small amount of spherical shapes (figure 4d). In this sample, Co₄S₃ nanorods have been detected with an average aspect ratio of 4.5 ± 0.8 nm. The average longest diagonal distance in the mixture of triangular, hexagonal and spherical particles is 25.5 ± 4.5 nm. When the precursor:OA ratio is increased to 1:100, the dominant shape of the nanoparticles is spherical, with an average diameter of 10.5 ± 2 nm (figure 4e). At the lowest amount of the precursor (precursor:OA = 1:200), there is a mix between irregular-shaped particles and nanorods, with an average diagonal of 15.9 ± 1 nm (figure 4f). This observation could be explained by the growth process involving a delicate balance between kinetic and thermodynamic control. At a high flux of monomer, anisotropic growth is facilitated (Li et al. 2003). Moreover, it has been suggested that the chemical potentials of nanocrystals are related to the formation of nanocrystals with different morphologies and sizes (Peng & Peng 2002). The chemical potential of the reaction environment is mainly determined by the monomer concentration at a fixed temperature. Therefore, when the concentration of precursor increases, the reaction system can deviate towards kinetic control, resulting in multiple shapes of nanoparticles.
being formed. When the OA amount increases to 1:100, there is competition between the binding mechanism of the capping agent and the growth process of the nanoparticles to prevent anisotropic growth (Winter et al. 2004).

To fully understand the effect of reaction time on the shape of the synthesized nanoparticles, the samples were monitored at different time intervals. Figure 4g–i shows Co$_4$S$_3$ nanoparticles at different reaction times after precursor injection. The product obtained after 10 min shows spherical nanoparticles with an average diameter of 2.6 ± 0.3 nm (figure 4g). When the reaction time increased to 20 min, the nanoparticles have grown to 5.2 ± 0.6 nm (figure 4h) and some irregular-shaped particles begin to form. With a reaction time of 30 min, the average maximum dimension further increases with a predominantly spherical shape. After 60 min, more irregular shapes with an average diagonal dimension of 16.8 ± 1.2 nm were produced (figure 4i). The formation of different structures with
different reaction times can be explained by an ‘Ostwald ripening process’ (Lee et al. 2003; Li et al. 2003; Murray et al. 1993). During the reaction procedure, a large number of nuclei were formed in a short time through a known Ostwald ripening process. As the reaction proceeds, the aggregate continuously grows in size and density to form spheres through the interaction between OA molecules and the nanoparticles by Van der Waals forces and intermolecular hydrogen bonds. Then, the assembled nanoparticles with a relatively large size could serve as crystal nuclei.

In succession, the particles with small size can dissolve and recrystallize because of their much higher surface free energy when compared with that of the larger ones. Consequently, some triangular, hexagonal and rod particles can be formed. However, in the middle of reaction, irregular-shaped nanoparticles together with spherical nanoparticles were observed. This could be explained by the competition between the binding mechanism of the capping agent and growth of the nanocrystal by the Ostwald ripening process. The Co$_4$S$_3$ nanoparticles were further studied by using HR-TEM. Although the XRD result shows a mixture of hexagonal and cubic Co$_4$S$_3$, each particle is of a single phase. Figure 5 shows the different shapes of individual particles in the samples. The HR-TEM images show clear lattice fringes for cobalt sulphide nanoparticles. The lattice spacing of 0.284 nm between adjacent lattice planes in figure 5a–e corresponds to the (222) reflection and the 0.228 nm spacing seen in figure 5f corresponds to the (331) reflection of cubic Co$_4$S$_3$. In the case of hexagonal Co$_4$S$_3$, particles are mostly trianularly faceted or spherical in shape. The lattice spacings are 0.293, 0.192 and 0.259 nm that respectively correspond to the (100), (102) and (101) reflections of hexagonal Co$_4$S$_3$ (figure 5f–h).

4. Conclusions

[Co{N(SCNMe$_2$)$_2$)$_3$}] (1) and [Co{N(SOCN$i$Pr$_2$)$_2$}$_2$] (2) have been synthesized and characterized. Thermolysis of these precursors in HDA, ODA or OA produced different phases as confirmed by powder XRD. TEM images showed triangular and spherical Co$_{1-x}$S nanoparticles from the thermolysis of complex 1 whereas spherical, rod, trigonal, pentagonal and hexagonal Co$_4$S$_3$ nanoparticles were obtained from complex 2 depending on the growth temperature and precursor concentration. The two different phases of cobalt sulphide obtained from precursor 1 and precursor 2 can also be related to the lower sulphur content in precursor 2, hence depositing a sulphur-deficient phase Co$_4$S$_3$.

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