Polyhedron 56 (2013) 62-70

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis of multi-podal CdS nanostructures using heterocyclic dithiocarbamato complexes as precursors

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ARTICLE INFO

Article history: Received 30 October 2012 Accepted 5 March 2013 Available online 28 March 2013

Keywords: CdS nanostructures Dithiocarbamates

ABSTRACT

Bis(dipiperidinyldithiocarbamato)cadmium(II) (1) and *bis*(ditetrahydroquinolinyldithio-carbamato)cadmium(II) (2) were used as precursors for the synthesis of oleylamine (OA), decylamine (DA) and dodecylamine (DDA) capped CdS nanoparticles. The optical properties of these particles have been studied. The absorption spectra for the amine capped CdS particles are blue shifted in relation to the bulk material. The corresponding photoluminescence spectra show a narrow band edge emission. High quality crystalline CdS particles of different shapes, ranging from short nanorods and elongated nanorods (rods, bipods, tripods and tetrapods) to nanocubes were obtained when the reaction temperature was varied between 180 and 270 °C. A decrease in the length of the rods and bipodal nanoparticles was observed with an increase in the length of the chain of the amine (capping agent) used. The p-XRD patterns revealed the hexagonal phase of CdS to be dominant in all the samples. Infra-red studies suggest that the mode of bonding of the amines (oleylamine, decylamine and dodecylamine) on the CdS nanoparticle surfaces is through electron donation from the nitrogen atoms.

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1. Introduction

The syntheses and applications of semiconductor nanomaterials have been the subject of intense research during the past two decades. Synthetic routes to nanostructured materials are generally divided into physical and chemical methods. The aim is to produce particles in the nanosize regime which are crystalline and regular in both size and shape. The ability to manipulate the size and shape of the particles has become a niche focus area in the field. This control will assist workers to optimally harness the unique properties of materials for applications. Cadmium sulfide, a II–VI type semiconductor, is a good example of a material whose size and shape can be manipulated by variation of the reaction conditions in the synthetic methodology [1–5].

The thermolysis of metal and chalcogenide sources in coordinating solvents is a common route to semiconductor nanomaterials. The so called 'hot injection' method allows for the manipulation of the capping ligands, ligand–solvent pair, reactant concentration and reaction temperature to control particle growth and the final morphology. Initially, highly reactive and toxic precursors, such as dimethylcadmium [6], *bis*(trimethylsilyl)sulfur [7], or trioctylphosphine sulfide [7,8], were the main sources of cadmium and sulfur for the synthesis of CdS nanoparticles. Later, less harmful cadmium sources such as CdCl₂ [8,9], Cd-oleate [10], or CdO [7,11], and sulfur precursors such as dodecanthiol [10], a solution of elemental sulfur in oleylamine [9], or in octadecene [11] were employed. A related method is the use of single source precursors incorporating the elemental constituents as starting materials. In these high temperature thermolyses or hot injection routes, the precursor is introduced into the hot solvent. There is a short burst nucleation, followed by slow growth and annealing. The separation between nucleation and growth stages facilitates shape control. The final shape, size, size-distribution and lattice type are determined based on the cumulative effects of nucleation and growth phases. Particles synthesized by this method exhibit excellent crystallinity and monodispersity.

Various classes of inorganic compounds have been used as precursors to CdS nanoparticles. There is a substantial body of work on the use of dithiocarbamato complexes of cadmium as single source precursors to CdS [12–17]. Related compound classes such xanthates [18–20], thioureas [21–25] and thiosemicarbazides [26] have also been extensively reported. Recently our group revisited the use of dithiocarbamato complexes as starting materials for CdS and PbS nanoparticles [3,5,14,27]. We found very interesting results when heterocyclic dithiocarbamato complexes such as cadmium and lead piperidinyl and tetrahydroquinolinyl





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^{0277-5387/\$ -} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2013.03.027

dithiocarbamates were used as precursors for CdS or PbS nanoparticles. By changing the reaction temperature and reactant concentration, particles in the shape of spheres, rods and cubes were formed. In this work we report the synthesis of anisotropic CdS nanoparticles by the thermolysis of heterocyclic dithiocarbamate complexes in decylamine (DA), dodecylamine (DDA) and oleylamine (OA) at various reaction temperatures.

2. Material and methods

2.1. Chemicals

Decylamine (DA), dodecylamine (DDA), oleylamine (OA), toluene, tri-octylphosphine (TOP) 90%, 1,2,3,4-tetrahydroquinoline 98% (Aldrich), piperidine 99% (Sigma–Aldrich), petroleum ether, methanol 99.5%, dichloromethane, carbon disulfide 99.5%, sodium hydroxide 98%, cadmium chloride monohydrate 99% and acetone (Merck) were used as purchased without any further purification.

2.2. Synthesis of the precursors

2.2.1. Preparation of the ligands

Carbon disulfide (6.0 mL, 0.1 mol) was added in small portions to an equimolar mixture of sodium hydroxide (4.0 g, 0.1 mol) and the corresponding amine (piperidine/tetrahydroquinoline, 0.1 mol) and cooled in an ice bath at 0 °C. After 15 min, the solidified mass was then dried in air and recrystallised in a mixture of acetone/petroleum ether. The product was collected and washed with chloroform and suction dried.

Na(pip-dtc), yield: 90%. ¹H NMR (400 MHz, DMSO-d₆) δ : 1.41 (m, 2H, 3-CH₂), 1.53 (t, 2H, 4-CH₂), 4.28 (t, 2H, 2-CH₂). IR (cm⁻¹, ATR): 3367 *v*(O–H); 967 *v*(C=S); 1468 *v*(C=N). Microanalysis, Calc. for C₆H₁₄NS₂O₂Na: C, 32.87; H, 6.44; N, 6.39. Found: C, 32.57; H, 6.29; N, 5.96%.

Na(thq-dtc), yield: 62%. ¹H NMR (400 MHz, CD₃OD) δ : 2.07 (m, 2H, 3-CH₂), 2.73 (t, 2H, 4-CH₂), 4.58 (t, 2H, 2-CH₂), 7.08–7.85 (m, 4H, Ar–H). IR (cm⁻¹, ATR): 3324 v(O–H); 967 v(C=S); 1485 v(C=N). Microanalysis, Calc. for C₁₀H₁₈NS₂O₄Na: C, 39.59; H, 5.98; N, 4.62. Found: C, 39.15; H, 5.94; N, 4.27%.

2.3. Preparation of the complexes

Cadmium chloride (5.0 mmol) was dissolved in distilled water (25.0 mL) and added dropwise to the corresponding solution of the dithiocarbamate ligand (10.0 mmol) in water and cooled in an ice bath at 0 °C. The reaction mixture was stirred for 1 h, and the precipitate formed was filtered, washed with excess distilled water and dried overnight in an oven at 70 °C.

2.3.1. Complex 1

 $\begin{bmatrix} Cd(pip-dtc)_2 \end{bmatrix} (pip = piperidinyl and dtc = dithiocarbamato), yield: 82%. ¹H NMR (400 MHz, CDCl_3) &: 1.63 (m, 8H, 3-CH_2), 1.73 (t, 4H, 3-CH_2), 4.13 (t, 8H, 2-CH_2). IR (cm⁻¹, ATR): 3324 v(O-H); 967 v(C=S); 1485 v(C=N); 388 v(Cd-S). Microanalysis, Calc. for C₁₂H₂₀N₂S₄Cd: C, 45.40; H, 3.81; N, 5.29. Found: C, 45.57; H, 3.61; N, 5.73%. \\ \end{bmatrix}$

2.3.2. Complex 2

[Cd(thq-dtc)₂] (thq = tetrahydroquinoliny), yield: 71%. ¹H NMR (400 MHz, CDCl₃) δ : 1.99 (m, 4H, 3-CH₂), 2.71 (t, 4H, 4-CH₂), 4.24 (t, 4H, 2-CH₂), 7.18–7.86 (m, 8H, Ar–H). IR (cm⁻¹, ATR): 3324 ν (O–H); 967 ν (C=S); 1485 ν (C=N); 365 ν (Cd–S). Microanalysis,







Fig. 2. (i) UV–Vis and (ii) PL spectra of CdS nanoparticles synthesised using Cd(pip-dtc) complex at 180 $^{\circ}$ C in (a) OA, (b) DA and (c) DDA.



Fig. 3. TEM and corresponding HRTEM image of CdS nanoparticles synthesised at 180 °C using [Cd(pip-dtc)₂] complex in (a) OA, (c) DDA and (e) DA.

Calc. for $C_{20}H_{20}N_2S_4Cd:$ C, 39.51; H, 5.98; N, 4.62. Found: C, 39.15; H, 5.94; N, 4.27%.

The structures of the complexes are shown in Fig. 1.

2.4. Synthesis of oleylamine (OA) capped CdS nanoparticles

A mass of 0.5 g (1.2 mmol) of the $[Cd(pip-dtc)_2]$ complex was dissolved in 6.0 mL of tri-*n*-octylphosphine (TOP). The solution was injected into 6.0 g (22.4 mmol) of hot oleylamine (OA) in a three-necked flask at 180 °C. The solution turned to a yellowish orange color and a drop in temperature of 32 °C was observed. The reaction was allowed to stabilize at 180 °C. After a reaction time of 1 h, aliquots of samples were taken and methanol was added, resulting in the formation of a flocculent precipitate. The precipitate was separated by centrifugation and then dispersed in toluene to give yellowish orange OA-capped CdS nanoparticles. The reaction was repeated at a reaction temperature of 270 $^{\circ}$ C. The above reaction procedure was then repeated using the [Cd(thq-dtc)₂] complex.

2.5. Synthesis of decylamine (DA) capped CdS nanoparticles

A mass of 0.5 g (1.2 mmol) of the $[Cd(pip-dtc)_2]$ complex was dissolved in 6.0 mL of TOP. The solution was injected into 6.0 g (38.1 mmol) of the hot DA in a three-necked flask at 180 °C. The solution turned a yellowish orange color and a drop in temperature of 25 °C was observed. The reaction was allowed to stabilize at 180 °C. After the reaction time of 1 h, aliquots of samples were taken and methanol added, resulting in the formation of a flocculent precipitate. The precipitate was separated by centrifugation, and dispersed in toluene to give yellowish orange DA-capped CdS nanoparticles. The reaction was repeated at a reaction temperature

Table 1

Absorption band edge, photoluminescence emission maxima and particle dimensions for CdS nanoparticles synthesized from [Cd(pip-dtc)₂] and [Cd(thq-dtc)₂] under various conditions.

	temp. (*C) Capping group	Absorption band edge (nm)	PL emission max (nm)	Particle shape/size (nm) l = length, $b = $ breadth, $s = $ size
[Cd(pip-dtc) ₂] 180	OA	493	481	rods: $l = (41.07 \pm 4.72), b = (3.66 \pm 0.45)$
				bipods: $l = (29.76 \pm 4.91), b = (1.55 \pm 0.27)$
[Cd(pip-dtc) ₂] 180	DA	506	485	rods: $l = (38.01 \pm 5.33), b = (6.90 \pm 0.33)$
				bipods: $l = (33.33 \pm 9.82), b = (6.90 \pm 0.33)$
				tripods: $l = (29.28 \pm 3.50), b = (7.43 \pm 0.35)$
[Cd(pip-dtc) ₂] 180	DDA	511	490	rods: $l = (28.42 \pm 4.21), b = (5.36 \pm 0.21)$
				bipods: $l = (29.47 \pm 4.21), b = (6.84 \pm 1.29)$
				tetrapods: <i>l</i> = (11.67 ± 6.50), <i>b</i> = (4.44 ± 4.00)
[Cd(pip-dtc) ₂] 270	OA	517	472	rods: $l = (35.78 \pm 3.94), b = (16.83 \pm 2.10)$
				bipods: $l = (42.10 \pm 6.44), b = (12.49 \pm 2.18)$
				tripods: <i>l</i> = (28.41 ± 4.20), <i>b</i> = (20.52 ± 3.49)
[Cd(pip-dtc) ₂] 230	DA	529	496	Rods: <i>l</i> = (19.50 ± 4.30), <i>b</i> = (6.00 ± 1.22)
				bipods: $l = (17.50 \pm 3.53), b = (5.62 \pm 1.08)$
				tripods: $l = (12.50 \pm 4.67), b = (6.25 \pm 1.25)$
[Cd(pip-dtc) ₂] 230	DDA	554	495	rods: $l = (15.55 \pm 2.22), b = (6.11 \pm 1.41)$
			570	bipods: $l = (17.22 \pm 2.72), b = (6.94 \pm 1.24)$
				tripods: $l = (13.33 \pm 4.78), b = (7.50 \pm 2.08)$
$[Cd(thq-dtc)_2]$ 180	OA	491	479	rods: <i>l</i> = (21.00 ± 1.00), <i>b</i> = (2.00 ± 0.90)
			628	elongated tetrapods: $l = (24.00 \pm 5.50), b = (4.00 \pm 1.25)$
$[Cd(thq-dtc)_2]$ 270	OA	524	472	cubes: $s = (13.25 \pm 1.95)$
$[Cd(thq-dtc)_2]$ 230	DA	540	487	rods: <i>l</i> = (15.08 ± 1.68), <i>b</i> = (9.37 ± 1.80)
			568	
$[Cd(thq-dtc)_2]$ 230	DDA	575	486	rods: $l = (17.39 \pm 1.66), b = (9.52 \pm 1.66)$
			568	

of 230 °C. The same reaction procedure was repeated using the $[Cd(thq-dtc)_2]$ complex.

2.6. Synthesis of dodecylamine (DDA) capped CdS nanoparticles

A mass of 0.5 g (1.2 mmol) of the $[Cd(pip-dtc)_2]$ complex was dissolved in 6.0 mL of TOP. The solution was injected into 6.0 g (32.3 mmol) of hot DDA in a three-necked flask at 180 °C. The solution turned a yellowish orange color and a drop in temperature of 27 °C was observed. The solution was allowed to stabilize at 180 °C. After a reaction time of 1 h, aliquots of samples were taken and methanol added, resulting in the formation of a flocculent precipitate. The precipitate was separated by centrifugation, and dispersed in toluene to give yellowish orange DDA-capped CdS nanoparticles. The reaction procedure was repeated with the $[Cd(thq-dtc)_2]$ complex.

2.7. Instrumentation

Microanalysis was performed on a Perkin-Elmer automated model 2400 series II CHNS/O analyzer. Infrared spectra were recorded on a Bruker FT-IR tensor 27 spectrophotometer directly on small samples (10 mg) of the compounds in the range 200–4000 cm⁻¹. The ¹H NMR spectra of both the ligands and the metal complexes were obtained using a Bruker advance III 400 MHz spectrophotometer. The crystalline phase was identified by X-ray diffraction (XRD), employing a scanning rate of 0.05° min⁻¹ in a 2 θ range from 20° to 80°, using a Bruker AXS D8 diffractometer equipped with nickel filtered Co Ka radiation $(\lambda = 1.5418 \text{ Å})$ at 40 kV, 40 mA and at room temperature. The morphology and particle sizes of the samples were characterized by a JEOL 1010 TEM with an accelerating voltage of 100 kV, Megaview III camera and Soft Imaging Systems iTEM software. The detailed morphological and structural features were investigated using HRTEM images with a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. A Varian Cary 50 Conc UV-Vis spectrophotometer was used to carry out the optical measurements and the samples were placed in silica cuvettes (1 cm path length), using toluene as a reference solvent. A Perkin Elmer, LS 55 Luminescence spectrometer was used for recording the photoluminescence spectra.

3. Results and discussion

3.1. Characterization of the precursors

Elemental analyses revealed that the ligands and the complexes synthesized were pure and agreed with the proposed formulae. The precursors were obtained in good yield with a simple reaction procedure. The piperidine dithiocarbamate ligand and its corresponding cadmium complex were obtained as white precipitates, whilst the tetrahydroquinoline dithiocarbamate ligand was obtained as yellow microcrystals and its cadmium complex as a pale yellow powder. The compounds are air stable, easy to synthesize and soluble in some organic solvents, such as chloroform.

The FT-IR spectra of the hydrated sodium salts of the dithiocarbamate ligands showed very broad bands in the 3500-3000 cm⁻¹ region, typical of OH of water molecules. The C-N stretching vibration usually appears in dithiocarbamates as a strong band around 1500 cm⁻¹. The position of this band is indicative of the degree of the double bond character in the C–N bond [28] (v(C=N) = 1690– 1640; $v(C-N) = 1350-1250 \text{ cm}^{-1}$). The IR spectra of the *bis*(ditetrahydroquinolinyldithiocarbamato)cadmium(II) and bis(dipiperidinyldithiocarbamato)cadmium(II) complexes showed v(C=N)bands at 1446 and 1483 cm⁻¹, respectively, indicating partial double bond character. The v(C-N) band is higher for bis(dipiperidinyldithiocarbamato)cadmium (II) than for bis(ditetrahy droquinolinvldithiocarbamato)cadmium(II). This may be due to the electron withdrawing resonance effects of the phenyl ring in tetrahydroquinolinedithiocarbamate, resulting in a decrease in the double bond character of the C-N bond [29]. The v(C=S) band is observed in the 999–975 $\rm cm^{-1}$ range in the spectra of the sodium salts of the ligands. The upward shift of the band for the dithiocarbamate from that of the free ligand, together with a strong band (or two very close bands) attributed to v(C-S), is indicative of a bidentate or slightly anisobidentate dithiocarbamate [30]. In the far IR region, a new additional band, absent in the spectra of the ligands, is observed in the $365-388 \text{ cm}^{-1}$ region, which possibly corresponds to v(Cd-S).

3.2. Synthesis of CdS nanoparticles

Long chain amines are found to be suitable surfactants for II–VI semiconductor nanomaterials. The as-prepared unshelled CdSe nanoparticles with long chain primary amines were found to have emission quantum yields of 60%, without the need for an inorganic shell [31]. In this work we decided to explore the use of long chain amines, such as hexadecylamine (HDA), oleylamine (OA), decylamine (DA) and dodecylamine (DDA), as capping groups for CdS nanoparticles.

3.3. Synthesis of CdS from the cadmium piperidine dithiocarbamato complex

In our previous work [5,15], we reported the synthesis of HDA and TOPO-capped CdS nanoparticles using *bis*(dipiperidinyldithio-carbamato)cadmium(II) and *bis*(ditetrahydroquinolinyldithiocarbamato)cadmium(II) complexes. The thermolysis of the precursors at moderate reaction temperatures (140 and 180 °C) using HDA as the capping group resulted in elongated and spherically shaped particles [5,15]. At a higher reaction temperature (240 °C), large faceted CdS particles in the shape of hexagons and cubes were formed [15]. In this work we have used the same precursors, but changed the length of the chain of the linear shaped amine, using OA, DA and DDA as the passivating group, at reaction temperatures of 180, 230 and 270 °C.



Fig. 4. TEM and corresponding HRTEM image of CdS nanoparticles synthesised using [Cd(pip-dtc)₂] with 3 g of (a) OA at 270 °C and with 6 g of (c) DA and (e) DDA.

The *bis*(dipiperidinyldithiocarbamato)cadmium(II) complex was thermolysed in OA at 180 °C. The absorption and photoluminescence spectra of the OA capped CdS nanoparticles are shown in Fig. 2a. The absorption band edge is sharp, with a band gap positioned at 493 nm. The photoluminescence spectrum shows two peaks (Fig. 2a). The first narrow emission peak has a maximum at 481 nm, whereas a broad weak emission peak is observed in the 550–700 nm region. The latter emission is due to trap emission, observed in poorly passivated surfaces and/or defects in the crystal lattice.

A similar reaction procedure was adopted for the particles synthesized in DA and DDA. The absorption and photoluminescence spectra of the DA and DDA capped CdS nanoparticles at 180 °C are shown in Fig. 2b and c. The absorption spectra show distinct band edges at 506 and 511 nm for the DA and DDA capped CdS nanoparticles, respectively. The positions of the band edges show a slight blue shift from bulk CdS (515 nm). The corresponding photoluminescence spectra (Fig. 2b and c) show narrow emission peaks with the emission maxima at 485 (DA) and 490 nm (DDA).

The TEM and HRTEM images of the OA, DA and DDA capped CdS nanoparticles synthesized at 180 °C are shown in Fig. 3. All three capping groups led to elongated particles in the form of rods, bipods, tripods and tetrapods, the dimensions of which are shown in Table 1. There is a decrease in the length of the rods and bipods as we increase the length of the carbon chain from DA ($l = 38.01 \pm 5.33$ nm) to DDA ($l = 28.42 \pm 4.21$ nm).

In our previous work with HDA (which is longer than DDA) at 180 °C, we obtained shorter rods of length ($l = 19.11 \pm 7.29$ nm) [5]. An aspect ratio of 11.22, 5.50 and 5.30 is obtained for OA, DA and DDA respectively. The HRTEM image for the OA capped CdS shows an elongated particle with distinct lattice fringes (Fig. 3b) The *d*-spacing of 3.3 Å corresponds to the [001] plane of hexagonal CdS. A CdS particle in the form a tetrapod is observed in the HRTEM image of the DDA capped CdS (Fig. 3d).

When the reaction temperature is increased to 230 °C for DA and DDA, and 270 °C for the OA capped CdS nanoparticles, a change in the optical properties of the CdS nanoparticles is observed. The absorption spectra are broader and there is a general decrease in the intensity of the emission peaks and a shift to longer wavelengths (Table 1). This change is due to the change in particle size and size distribution due to the higher reaction temperatures. The higher temperature also favors a reduction of surface defects through annealing. The TEM and HRTEM images (Fig. 4) show that the breadth of the nanorods increased while the length decreased. Short rods, bipods and tripods of CdS are clearly visible, whose dimensions are presented in Table 1. The crystallinity of the particles is confirmed, with distinct lattice fringes observed in the HRTEM images. The HRTEM images of the OA and DA capped CdS show the presence of tetrapod shaped particles (Fig. 4b and d). CdS nanoparticles with the tetrapod morphology are achieved through the formation of a zinc blende seed at a relatively low temperature, allowing growth along the four [111] faces, forming wurtzite arms. There is a separation angle of 113 °C between the arms. In Fig. 4f, a bipodal structure is visible with a zinc blende core, having a lattice spacing of 0.29 nm, corresponding to the [200] lattice plane. The two side arms have a lattice spacing of 0.34 nm, assigned to the [002] lattice planes of wurtzite CdS.

The X-ray diffraction (XRD) spectra for the amine capped CdS are shown in Fig. 5. The (110), (103) and (112) planes, indexed to wurtzite CdS, are present in the diffraction patterns. The sharp [002] planes, observed for all samples, are consistent with the preferential [001] growth direction in anisotropic CdS nanoparticles. There is evidence of diffraction from the zinc blende seed. The [103] plane for pure wurtzite is normally more intense than the [110] and [112] plane. These [110] and [112] planes could also correspond to the [220] and [331] planes of the zinc blende



Fig. 5. XRD patterns of CdS nanoparticles synthesised using [Cd(pip-dtc)₂] in(a) OA at 270 °C, (b) DDA at 230 °C and (c) DA at 230 °C.



Fig. 6. (a) UV–Vis and (b) PL spectra of CdS nanoparticles synthesised at 180 $^{\circ}$ C using [Cd(thq-dtc)₂] in OA.

structure. However the weaker [102] plane confirms the wurtzite phase is dominant.

3.4. Synthesis of CdS nanoparticles from the cadmium tetrahydroquinolinedithiocarbamate complex

The CdS nanoparticles were synthesized in OA at 180 °C using the bis(ditetrahydroquinolinyldithiocarbamato)cadmium(II) complex. The optical spectrum of the OA capped CdS using this precursor is similar to that of the OA capped particles synthesized from the *bis*(dipiperidinyldithiocarbamato)cadmium(II) complex. The UV-Vis spectrum shows a sharp absorption band edge of 491 nm (Fig. 6a). Two peaks are observed in the photoluminescence spectrum, a narrow peak with an emission maximum at 479 nm and a second deep trap peak with a maximum at 628 nm (Fig. 6b). The TEM image of the OA capped CdS synthesized at 180 °C shows a mixture of tripods and tetrapods, similar to those obtained using the piperidinyldithiocarbamato complex at the corresponding temperature. However when the reaction temperature is increased to 270 °C, the morphology of the particles changes drastically. The TEM image of the OA capped CdS (Fig. 7c) shows a mixture of cubic- and hexagonally shaped particles. The average size of the cubes is 13.25 ± 1.95 nm. A well-defined cube shaped CdS particle with distinct lattice fringes is observed in the HRTEM image (Fig. 7d). In our previous work on CdS using bis(ditetrahydroquinolinyldithiocarbamato)cadmium(II) as a precursor, thermolysed in HDA at 240 °C, we obtained large faceted CdS particles having hexagonal, cubic and other irregular shapes [5].



Fig. 7. TEM and corresponding HRTEM images of OA-capped CdS nanoparticles synthesised using [Cd(thq-dtc)₂] at (a) 180 and (c) 270 °C.

It is evident that the higher temperature favors the formation of large close to cubic particles when using this class of precursor. We have also synthesized CdS nanoparticles using the *bis*(dite-trahydroquinolinyldithiocarbamato)cadmium(II) pre-cursor therm olysed in DA and DDA at a reaction temperature of 230 °C. The TEM images of the CdS particles synthesized in DA (Fig. 8a) show short nanorods with an average length of 15.08 ± 1.68 nm and breadth of 9.37 ± 1.80 nm. The DDA capped particles have a similar morphology with a length of 17.39 ± 1.66 nm and breadth of 9.52 ± 1.66 nm (Fig. 8c). A single crystalline particle in the form of a rectangle is observed in the HRTEM image of the DA capped CdS particles (Fig. 8d).

Ab initio calculations suggested that the mode of bonding of amines to the nanoparticle surfaces is through the lone pair of electrons on the nitrogen atom [32]. There is an argument that the acidic proton in the NH₂ group on a primary amine can coordinate to a surface metal site [33]. The use of tertiary amines in nanoparticle synthesis does appear to contradict this [34,35], and it is possible that the coordination of amines to nanoparticle surfaces may actually occur through both the lone pair of electrons and the protons. FTIR spectra of oleylamine-capped FePt particles confirm the presence of N-H and suggested that oleylamine appeared to bind through electron donation from the nitrogen atom [36]. The capping agents used in our work (oleylamine, decylamine and dodecylamine) are all primary amines. The IR spectra of the OA-, DA- and DDA-capped CdS nanoparticles are shown in Fig. 9. All three show the same peaks, with some differences in the level of their intensity at some wavenumbers. The peaks observed below 300 cm^{-1} are characteristic of the Cd–S bond. The C–H stretching is observed in the range 2911–2914 cm⁻¹. The peak at 3229 cm⁻¹ is attributed to the N–H stretching, thus confirming the presence of N-H and indicating that oleylamine, decylamine and dodecylamine appear to bind through electron donation from the nitrogen atom, as reported previously [36].

3.5. Branched growth

After the formation of a crystalline seed, the growth process occurs through a delicate balance between kinetic and thermodynamic preferences [37]. Factors such as reaction temperature and precursor temperature will determine the growth path. It has been shown that high temperatures and low precursor concentrations favor isotropic structures [38]. These structures are in the form of perfect or quasi-spheres. At low reaction temperatures and high precursor concentrations the growth path is kinetically driven, favoring the formation of anisotropic structures in the form of rods or branched structures. In our work we observed that there is a difference in the dimensions of the amine capped CdS obtained at different reaction temperatures using the $[Cd(pip-dtc)_2]$ complex. At reaction temperatures of 180 °C the average length of the rods in the form of bipods, tripods and tetrapods for the OA, DA and DDA capped CdS particles is 26.91 ± 3.64 nm. When the temperature is increased to 230 °C (DA and DDA) and 270 °C for the OA capped CdS, shorter and broader branched rods (av. length 22.43 ± 4.09 nm and breadth 9.81 ± 1.78 nm) are observed. A similar trend is observed when [Cd(thq-dtc)₂] is thermolysed in OA. At 180 °C narrow branched CdS particles in the form of bipods and tetrapods are observed, however when the temperature is increased to 270 °C cube shaped particles are observed. The DA and DDA capped particles obtained at 230 °C are also large faceted particles. This trend has been previously observed for oleylamine capped CdS nanoparticles synthesized at 175 and 100 °C. At 175 °C ellipsoidal particles were observed, but at the lower temperature of 100 °C rods, bipods, tripods and tetrapods were obtained. It is interesting to note that we have observed branched structures of CdS at relatively high reaction temperatures (230 and 270 °C) when the bis(dipiperidinyldithiocarbamato)cadmium(II) complex was thermolysed in all three amines. There have been no other reports of branched CdS at these high temperatures. The



Fig. 8. TEM and corresponding HRTEM images of CdS nanoparticles synthesised at 230 °C using [Cd(thq-dtc)₂] in (a and b) DA and (c and d) DDA.



Fig. 9. IR spectra of CdS nanoparticles synthesised using $[Cd(pip-dtc)_2]$ in (a) OA, (b) DA and (c) DDA.

reaction temperature of 180 °C is also relatively high, producing branched shaped particles without the addition of a shape directing agent. There is also no discernable difference in the morphology of the particles with respect to the capping group.

4. Conclusions

Two heterocyclic dithiocarbamatocadmium(II) complexes have been thermolysed in oleylamine, decylamine and dodecylamine at various reaction temperatures (180, 230 and 270 °C) to give branched shaped CdS nanorods. The optical properties of the materials under all reaction conditions confirmed the quantum confined nature of the particles. We found that at relatively high reaction temperatures branched particles in the form of tetrapods were formed when the *bis*(dipiperidinyldithiocarbamato)cadmium(II) complex was thermolysed in all three amines, whereas the bis(ditetrahydro- quinolinyldithiocarbamato)cadmium (II) complex gave cubic shaped particles at high reaction temperatures. A decrease in the length of the rods, and the bipodal nanoparticles was observed with an increase in the length of the chain of the alkylamine. The dominant hexagonal phase in both is confirmed by X-ray diffraction measurements. Infra-red studies indicate that the amines used in our work as capping agents bind on the surface of the CdS nanoparticles through electron donation from the nitrogen atoms.

Acknowledgements

This work was supported by the Department of Science and Technology (DST) and National Research Foundation (NRF) of South Africa through the DST/NRF South African Research Chairs Initiative (SARCHi) program. Ms. L.D. Nyamen also acknowledges the Organization for Women Scientists for the Developing World (OWSDW) formerly TWOWS for a Sandwich Postgraduate Fellowship. The authors also acknowledge the Centre for Electron Microscopy, University of Kwa-Zulu Natal for the TEM and National Centre for Nano-structured Materials (NCNSM), CSIR, Pretoria for HRTEM measurements.

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