



Synthesis of hexadecylamine capped CdS nanoparticles using heterocyclic cadmium dithiocarbamates as single source precursors

Thandeka Mthethwa^a, V.S.R. Rajasekhar Pullabhotla^{a,*}, Phumlani S. Mdluli^a, James Wesley-Smith^b, Neerish Revaprasadu^{a,*}

^a Department of Chemistry, University of Zululand, Kwa-Dlangezwa, Private Bag X1001, 3886, South Africa

^b Electron Microscope Unit, University of KwaZulu-Natal, Chiltern Hills, Westville Campus, Durban, Private Bag X 54001, 4000, South Africa

ARTICLE INFO

Article history:

Received 20 March 2009

Accepted 3 July 2009

Available online 14 July 2009

Keywords:

Single source precursors

Dithiocarbamates (DTC)

Hexadecylamine (HDA)

Tri-octylphosphine (TOP)

CdS nanoparticles

ABSTRACT

Heterocyclic cadmium dithiocarbamates, $[\text{Cd}(\text{S}_2\text{CNC}_5\text{H}_{10})_2]$ and $[\text{Cd}(\text{S}_2\text{CNC}_9\text{H}_{10})_2]$ were synthesized. The complexes were thermolysed in hexadecylamine (HDA) to give HDA capped CdS nanoparticles. A combination of close to spherical, rod, bipods and tripods was obtained by varying the reaction parameters such as precursor concentration and temperature. The optical properties and X-ray diffraction studies of the particles are also reported.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Semiconductor nanoparticles belonging to groups II–VI and III–V have been the subject of great interest due to their uses in various applications such as light emitting applications, photoelectric conversion in solar cells and other optical devices [1]. CdS is one of the metal chalcogenide materials which shows a variation in 1D morphology when the reaction conditions change (i.e. monomer concentration, reaction temperature and reaction time). Any combination of reaction conditions could lead to diverse shapes such as dots, rods, bipods, tripods, tetrapods and spindles [2].

The use of single source precursors containing both the metal and the chalcogenide source has been extensively studied as an effective route to semiconductor nanoparticles [3–5]. This method avoids problems associated with the use of toxic and volatile compounds at high temperatures and is known to produce nanomaterials of high quality. In particular cadmium or zinc dithio-/diselenocarbamates have proven to be very successful as precursors for the synthesis of CdS or ZnS nanoparticles [6]. Subtle changes in the substituents at the nitrogen of a diseleno- or dithiocarbamate can markedly affect the thermal decomposition of metal complexes used in the preparation of the metal chalcogenides. GC–MS studies have shown that the decomposition mechanisms of symmetrical diselenocarbamates produce selenium

clusters; however, the unsymmetrical diselenocarbamates produce only the metal selenide and organic by-products [7]. Other thiol based precursors such as xanthates [1,8], thioureas [9,10] and thiosemicarbazides [11] have also been extensively reported as suitable compounds for metal sulfide nanoparticles.

Very briefly the single source or ‘one-pot’ method involves the thermolysis of the precursor in a high boiling point coordinating solvent such as tri-*n*-octylphosphine oxide (TOPO) or hexadecylamine (HDA). When the precursor is added to the solvent, there is a short burst nucleation, followed by slow growth and annealing, consistent with an Ostwald ripening process. The coordinating solvent plays a major role in stabilizing the nanocrystalline colloidal dispersions and passivating the particle surface.

In this work we have used the cadmium piperidine dithiocarbamate (DTC), $[\text{Cd}(\text{S}_2\text{CNC}_5\text{H}_{10})_2]$ and cadmium tetrahydroisoquinoline dithiocarbamate, $[\text{Cd}(\text{S}_2\text{CNC}_9\text{H}_{10})_2]$ complexes as single source precursors for the synthesis of hexadecylamine capped CdS nanoparticles. The complexes were synthesized according to a method previously reported [12]. To our knowledge this is the first report of the use of a heterocyclic dithiocarbamate complex for the synthesis of CdS nanoparticles. HDA was used as the coordinating solvent in our study because it has been shown to decrease growth rate and particle size when used as capping agent and also to improve the photoluminescence quantum efficiency by effectively passivating the surface defect behaving as a non-radiative relaxation centre [13,14]. This is due to its high electron donating ability and high capping density as a result of its small stereochemical interference.

* Corresponding authors. Tel.: +27 35 902 6152; fax: +27 35 902 6568.

E-mail addresses: rajasekhar@yahoo.com (V.S.R. Rajasekhar Pullabhotla), nrevapra@pan.uzulu.ac.za (N. Revaprasadu).

2. Experimental

2.1. Materials and methods

Tetrahydroisoquinoline, piperidine, carbon disulfide, sodium hydroxide, cadmium chloride, hexadecylamine (HDA) (98%) and tri-octylphosphine (TOP) (90%) were purchased from Aldrich and were used as purchased. Toluene (BDH, 99%), methanol (BDH, 99.8%) and dichloromethane (BDH, >99%) were used as solvents without further purification.

2.2. Physical measurements

The C, H, N, S elemental analysis was carried out with Leco-CHNS 932 analyzer. Roughly 2.0 mg of sample was introduced into Ag capsule and was placed in a furnace, which was maintained at 800 °C. The products of combustion in the CHNS analysis (CO₂, H₂O and SO_x gases) were carried through the system by the He carrier. Adjustments for blank, calibration and weights were applied to the final integrated signal and the results were displayed as weight percentage of carbon, hydrogen, nitrogen and sulfur.

FT-IR spectra of various powder samples of ligands and complexes were recorded on a Bruker Tensor 27 spectrometer with a 4 cm⁻¹ resolution and 32 scans in the mid IR (200–4000 cm⁻¹) region. PL and UV-Vis absorption spectra were measured at room temperature with a Perkin Elmer LS 55 luminescence spectrometer and a Varian Cary 50 Conc UV-Vis spectrophotometer, respectively. Photoluminescence spectra were recorded by placing the sample in a quartz cuvette of 1 cm path length. The excitation wavelength for PL measurement was 400 nm. The samples were analyzed at a scan speed of 500 nm min⁻¹ within a scan range of 200–800 nm. UV-Vis spectra were recorded by placing the samples in a quartz cuvette of 1 cm path length at an absorption range of 200–800 nm with the scan rate of 600 nm min⁻¹. Toluene was used as a solvent (as reference in UV) in the measurements. Powder XRD patterns were recorded for all the samples in order to verify the formation and structure of materials. The dry samples were ground with the help of a mortar and pestle and the fine powder of nanoparticles was packed on the surface of a sample holder. The diffraction patterns were recorded in the high angle 2θ range of 10–80° using a Bruker AXS D8 Advance X-ray diffractometer, equipped with nickel filtered Co Kα radiation (λ = 1.5418 Å) at

40 kV, 40 mA and at room temperature. The scan speed and step size were 0.05° min⁻¹ and 0.00657, respectively. For the transmission electron microscopy (TEM and HRTEM) measurements, samples were prepared by placing a drop of dilute solution of nanoparticles on Formvar-coated grids (150 mesh). The samples were allowed to dry completely at room temperature and viewed using a JEOL 1010 TEM and JEOL 2100 HRTEM. Viewing was done at an accelerating voltage of 100 kV (TEM) and 200 kV (HRTEM), and the images were captured digitally using a Megaview III camera; stored and measured using Soft Imaging Systems ITEM software.

2.3. Preparation of ligands

A standard solution of NaOH 4 M (25.0 mL) was cooled in an ice bath and the corresponding secondary amine, piperidine or tetrahydroisoquinoline (25.0 mL) was added. To this suspended mixture in ice, CS₂ (7.0 mL) was added dropwise while stirring. The solution was allowed to stand for 1 h and the solidified mixture was dried in air. The solid was re-crystallised using 100.0 mL of dichloromethane and methanol (50:50 – v:v) mixture and was maintained at ice cold conditions overnight. The resultant precipitate was filtered and washed with excess dichloromethane.

C₁₀H₁₀NS₂Na: CHNS analysis: Calc.: C, 51.93; H, 4.36; N, 6.06; S, 27.72. Found: C, 51.58; H, 4.07; N, 5.85; S, 27.47%. Percentage yield: 54%; melting point: 137.8–138.2 °C. Significant IR bands: ν_(C-N): 1473 cm⁻¹; ν_(C-S): 949 cm⁻¹.

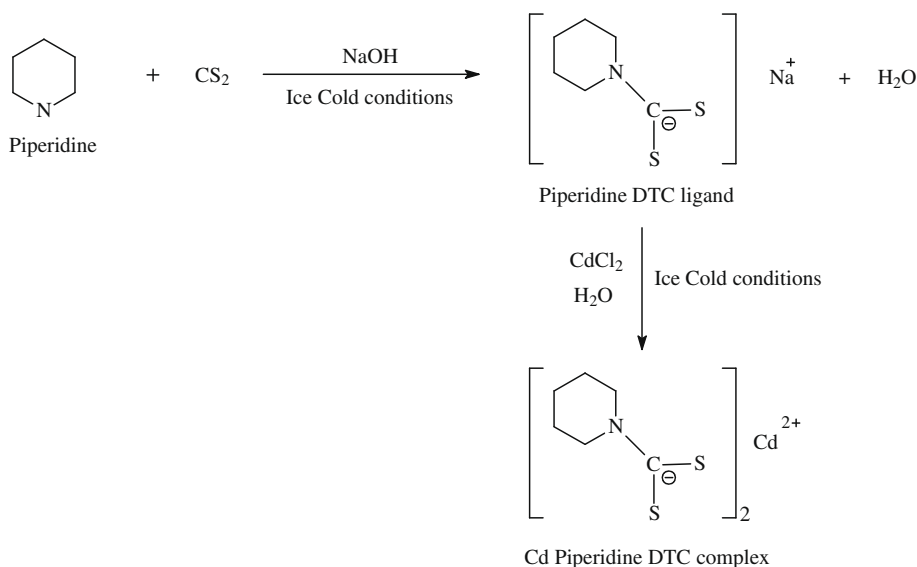
C₆H₁₀NS₂Na: CHNS analysis: Calc.: C, 39.32; H, 5.50; N, 7.64; S, 34.99. Found: C, 38.47; H, 5.98; N, 7.43; S, 34.51. Percentage yield: 58%; melting point: 133.2–135.4 °C. Significant IR bands: ν_(C-N): 1435 cm⁻¹; ν_(C-S): 958 cm⁻¹.

2.4. Preparation of complexes

2.4.1. Synthesis of [Cd (S₂CNC₅H₁₀)₂] (I)

A CdCl₂ solution, 10.0 mmol (25.0 mL) was added dropwise to the 25.0 mL solution of piperidine DTC ligand (5.0 mmol) at ice cold temperature (Scheme 1). The reaction was stirred for 1 h and the white precipitate formed was filtered, washed with distilled water and vacuum dried.

CHNS analysis: Calc.: C, 33.29; H, 4.66; N, 6.47; S, 29.62. Found: C 34.29; H, 4.56; N, 6.18; S, 29.47%. Percentage yield: 46%, melting



Scheme 1. Reaction scheme for the synthesis of Cd piperidine DTC complex.

Download English Version:

<https://daneshyari.com/en/article/1337541>

Download Persian Version:

<https://daneshyari.com/article/1337541>

[Daneshyari.com](https://daneshyari.com)