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Synthesis and structural characterization of CdS nanoparticles using nitrogen adducts of mixed diisopropylthiourea and dithiolate derivatives of Cd(II) complexes

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ABSTRACT

[Cd(diptu)$_2$(ced)], [Cd(diptu)$_2$(ced)(bpy)], [Cd(diptu)$_2$(ced)(phen)], (where diptu = diisopropyl thiourea; ced = 1-cyano-1-carboethoxy-lethylene-2,2′-dithiolate; bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline) have been prepared and used as single source precursors for the preparation of hexadecylamine capped CdS nanoparticles. The precursor complexes were characterized by elemental analysis, FTIR and TGA. The structural properties of the nanoparticles were investigated using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy techniques (SEM). The optical properties of the nanoparticles were studied using UV–Visible and photoluminescence spectroscopy. The XRD analysis showed that the nanoparticles were indexed to the hexagonal phase of CdS and the TEM results showed CdS nanoparticles with average crystallite sizes of 4.00–8.80 nm.

1. Introduction

Semiconductor nanocrystals have attracted immense interest due to their dimension dependent optical, electronic, magnetic, electrical and chemical properties, which are different from those of bulk

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materials [1–3]. Cadmium sulfide, with a band gap of (2.4 eV) [4], is one of the most important group of II-VI semiconductor with possible applications in solar battery [5], laser light emitting diodes [6], photocatalysis [7–9], non-linear optical materials and biological labels [10]. Different synthetic techniques such as colloidal precipitation [11], solvothermal [12], sonothermal [13], and thermolysis of single-source precursors [14,15] have been used to synthesize cadmium sulfide nanoparticles. Among these techniques, the use of single source precursors have been found effective for the synthesis of semiconductor nanoparticles [16,17]. Ligands play important role in the decomposition of the precursor compounds due to several properties such as volatility; basicity, induced inductive and mesomeric effect, number of donor atoms and the number of atoms which participate in coordinative bond [18]. Hence, this ultimately influences the decomposition profile of the compound and also enhances their use as precursor complex in the preparation of metal sulfide nanoparticles [19,20].

The aim of this work was to study the influence of 2,2′-bipyridine and 1, 10-phenanthroline ligands in the precursor complexes on the structural and optical properties of CdS nanocrystals. We report the synthesis and characterization of HDA-CdS nanoparticles obtained from the compounds [Cd(diptu)$_2$(ced)], [Cd(diptu)$_2$(ced)(bpy)], [Cd(diptu)$_2$(ced)(phen)] (where diptu=diisopropyl thiourea; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline) via single-source precursor method. To the best of our knowledge, this is the first report on the synthesis of CdS nanoparticles using the mixed ligands of diisopropyl thiourea and 1-cyano-1-carboethoxylethylene 2,2-dithiolate, with the 2,2′-bipyridine and 1,10-phenanthroline acting as Lewis bases in the formation of the adducts.

2. Materials and methods

2.1. Materials

Chloroform, methanol, diethyl ether, carbon disulfide, 1,4 dioxane, ethyl cyanoacetate, cadmium chloride, 2,2′-bipyridine, 1,10-phenanthroline, potassium hydroxide, tri-n-octylphosphine and hexadecylamine used in this work were all purchased from Merck. All the reagents were of analytical grade and used as supplied.

2.2. Techniques for characterization

The FTIR analysis of the metal complexes was done using KBr discs on a Perkin Elmer Paragon 2000 FTIR spectrophotometer, in the range 4000–370 cm^{-1}. Elemental analysis was carried out on a Flash EA Series 1112 CHNS analyzer. The thermogram was analyzed by using SDTQ 600 thermal instrument. Samples were heated in an alumina crucible at the rate of 10 min^{-1}and thermogram was recorded in the temperature range of 20 °C to 650 °C under nitrogen atmosphere. Scanning electron microscope images were analyzed using JOEL JSM-6390 LVSEM at a rating voltage of 15–20 kV. Samples for the SEM analysis were prepared by mounting the nanoparticles on a stub using carbon double-sided tape. The samples were coated with Au/Pd using the Eiko IB 3 Ion coater for better imaging. Absorption spectra of the precursor complexes and the nanoparticles were recorded using Perkin Elmer Lambda 25 spectrophotometer, in chloroform from 800 to 200 cm^{-1}. The photoluminescence measurement was done using a Perkin Elmer LS 45 fluorimeter, while powder X-ray diffraction patterns of the nanoparticles were recorded on a Bruker D8 Advanced, equipped with a proportional counter using Cu Kα radiation (λ = 1.5405 A, nickel filter).

2.3. Experimental

2.3.1. Synthesis of potassium 1-cyano-1-carboethoxylethylene-2,2′-dithiolate

Pulverized potassium hydroxide (10 mmol) was suspended in dioxane (50 mL). A solution of ethyl cyanoacetate (5 mmol) and carbon disulfide (5 mmol) in dioxane (25 mL) was added into the solution, with stirring in ice to maintain a temperature of 15–20 °C. After the addition, the suspension was stirred for another 20 min and diluted with 125 mL of ether. The yellow precipitate was filtered, washed with dioxane-ether (1:1), and dried in vacuo over NaOH and P_2O_5 [21,22].