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Colloidal synthesis of monodispersed ZnS and CdS nanocrystals from novel zinc and cadmium complexes

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ABSTRACT

Monodispersed spherical and hexagonal shaped ZnS and CdS nanocrystals respectively, have been synthesized using novel heteroleptic complexes of xanthate (S_2COBu) and dithiocarbamate ($S_2CNMePh$). The nanocrystals were prepared via colloidal route and stabilized in hexadecylamine (HDA). The morphology of the as-prepared nanocrystals was characterized using transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and powdered X-ray diffraction (p-XRD) analysis. An average diameter of 7.2 nm and 8.6 nm were obtained for the ZnS and CdS respectively. The optical properties of the nanoparticles studied by UV–vis and photoluminescence (PL) spectroscopy showed a blue shift in the absorption spectra, and band edge emission respectively.

1. Introduction

Semiconductor nanomaterials have unique optical and electronic properties for practical applications, and have attracted a lot of attention. Among various semiconductor materials, much effort

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has been made to fabricate group II–VI binary semiconductors which possess attractive optical properties [1–3]. This class of nanomaterials has drawn considerable interest for use in photovoltaic (PV) technology, photocatalysis, electroluminescent displays, and tunable emission properties [4–6]. The size, morphology and dimensionality of nano-structured materials can strongly affect their properties. Thus, different low-dimensional ZnS and CdS nanostructures have been prepared. Examples include ZnS and CdS quantum dots [7,8], CdS nanorods and nanospheres [9,10], and ZnS nanotubes [11], etc.

While nanomaterials have been generated by several physical methods, chemical methods are still the most widely used, because they provide better control as well as enable different sizes, shapes and functionalization [12]. The synthetic procedures employed generally attempt to control the particle morphology – size and shape. Thermal decomposition, in a coordinating medium, is one of the most efficient pathways for synthesizing the II–VI nanoparticles. In the thermolysis process, the precursor powder is heated so as to nucleate metal sulfide (MS) particles which are then grown to the desired size by controlled reaction of precursor molecules [13]. Suitable single-source precursors for MS (M = Zn or Cd) would contain direct metal–sulfur bonds. In our previous studies, we reported the suitability of N-alkyl-N-phenyl dithiocarbamato complexes of the group 12 for the production of MS nanoparticles [14,15]. However, relatively few reports exist on xanthates as precursors for nanoparticles synthesis [16]. One reason maybe because xanthates do not offer much options for derivatisation as found in the dithiocarbamates. We decided to investigate novel molecular precursor complexes based on mixed ligands of xanthate and dithiocarbamate, and to study the structural and optical properties of the ZnS and CdS nanoparticles obtained.

Xanthate and dithiocarbamato complexes are air-stable with reasonable volatility and are readily obtained in good synthetic yields. Barreca et al. [17,18] have prepared metal sulfide thin films (ZnS, CdS, ZnxCd1−xS) from single-source O-alkylxanthate precursors via CVD. CdS nanocrystals including nanorods and faceted nanoparticles have been synthesized via the thermolysis of cadmium ethylxanthate [19]. Good quality organically capped ZnS and CdS nanocrystals prepared from different Zn and Cd complexes of dithiocarbamates as precursors have been reported [20–22]. In addition to their appreciable volatility and stability to air and moisture, the presence of pre-formed M–S bonds and the absence of M–C bonds enable their clean conversion into the metal sulfide in an inert atmosphere [23]. In this study, we report the preparation of Zn(II) and Cd(II) complexes with xanthate and dithiocarbamate moiety, thermal decomposition to metal sulfide is described, and their use as single-source precursor to synthesize monodispersed ZnS and CdS nanocrystals is presented.

2. Experimental

2.1. Materials

All the chemicals used were of analytical reagent grade and used as such. Zinc(II) chloride, hydrated cadmium(II) chloride, methyl aniline, and carbon disulfide were obtained from Sigma Aldrich. *n*-Butanol, sodium/potassium hydroxides were purchased from Merck, SA.

2.2. Physical measurements

The spectral analyses of the ligand and complexes were recorded on Bruker alpha-P FT-IR spectrometer in the 500–4000 cm^{-1} range, and 600 MHz Bruker Avance III NMR spectrometers. Microanalyses were carried out with Elementar, Vario EL Cube, set up for CHNS analysis. The thermal decomposition study was performed on an SDTQ 600 Thermal instrument. 10–12 mg of samples were contained within alumina crucibles and heated at a rate of 10 °C min^{-1} from room temperature to 800 °C under flowing nitrogen. For the nanoparticles, the X-ray powder diffraction data were collected on a Röntgen PW3040/60 X'Pert Pro X-ray diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5405 A) at room temperature. TEM measurements were performed on a TECNAI G2 (ACI) instrument operated at an accelerating voltage of 200 kV. The absorption measurements were carried out using a PerkinElmer Lambda 20 UV–vis spectrophotometer at room temperature. Photoluminescence measurement was done on a PerkinElmer LS 55 luminescence spectrometer.