



Generalized chemical route to develop fatty acid capped highly dispersed semiconducting metal sulphide nanocrystals

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ARTICLE INFO

Article history:

Received 8 November 2011

Received in revised form 12 March 2012

Accepted 5 April 2012

Available online 13 April 2012

Keywords:

A. Semiconductors

B. Chemical synthesis

ABSTRACT

This work deals with the synthesis of highly dispersed semiconducting nanocrystals (NCs) of cadmium sulphide (CdS), zinc sulphide (ZnS) and lead sulphide (PbS) through a simple and generalized process using oleic acid (OA) as surfactant. To synthesize these NCs, metal-oleate (M–O) complexes were obtained from the reaction at 140 °C between metal acetates and OA in hexanes media. Subsequently, M–O complexes were sulphurized using thioacetamide at the same temperature. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) characterizations show that the synthesized products are of nanoscale-size with highly crystalline cubic phase. The optical absorption of OA-capped metal sulphide NCs confirms that their size quantization induced a large shift towards visible region. Photoluminescence (PL) spectrum of CdS NCs shows a broad band-edge emission with shallow and deep-trap emissions, while PL spectrum of ZnS NCs reveals a broad emission due to defects states on the surface. The thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy indicate that fatty acid monolayers were bound strongly on the nanocrystal surface as a carboxylate and the two oxygen atoms of the carboxylate were coordinated symmetrically to the surface of the NCs. The strong binding between the fatty acid and the NCs surface enhances the stability of NCs colloids. In general, this generalized route has a great potential in developing nanoscale metal sulphides for optoelectronic devices.

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1. Introduction

Colloidal sulphide NCs belonging to II–IV and IV–VI groups have attracted a surge of interest for their novel application in many possible technological fields, including biological labelling and bio-diagnostics, electroluminescent devices, photovoltaic devices, light-emitting diodes and lasers [1–4]. Since the properties of these NCs are dependent on their size and shape, it is necessary to tailor these two parameters with respect to their particular applications. As the size of the NCs decreases, the effect of their surface area becomes more significant because of the increase in the volume fraction of surface atoms with respect to the entire particle [5].

The development of a stable colloidal suspension of semiconducting NCs is highly challenging due to their high surface energy. Therefore, it is essential to use surfactants or other capping materials

during the chemical process to coat these NCs in order to prepare a well-dispersed and stable colloidal suspension in solvent media. Over the past few years, several groups have reported the synthesis of metal chalcogenides using various synthesis routes, including soft templates, such as liquid crystals and micelles [6–8], solventless synthesis [9], the thermolysis of metal–alkanethiolate precursors [10,11], the thermolysis of metal–oleylamine complexes [12], simple surfactant assisted solvothermal and hydrothermal routes [13,14], green chemical approaches [15], and thermolysis single-source precursors [16]. However, the above chemical routes are not applicable as a general route for the synthesis of metal sulphide NCs. Joo et al. [17] reported later a general route for the synthesis of metal sulphide NCs based on the thermolysis and sulphurization of metal–oleylamine complexes at around 220 °C. Also, Choi et al. [18] investigated a simple generalized fabrication route for monodispersed metal sulphide NCs using the thermolysis and sulphurization of M–O complexes in alkanethiol at 300 °C. More recently, Yu et al. [19] reported a general synthesis route based on the thermolysis of metal cysteinate at high temperature for the synthesis of metal sulphide NCs at large scale.

All of the synthesis routes mentioned above were based on the thermolysis of organometallic complexes at high temperature

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(200–300 °C). Bakshi et al. [20–22] have used low temperature synthetic routes to produce shape and size controlled PbS/Se and CuSe NCs using various capping materials, such as cationic twin-tail surfactants and bovine serum albumen. We report here the synthesis of semiconducting metal sulphide NCs through the sulphurization of their M–O complexes. This generalized process is simple and cost effective because it produces metal sulphide NCs at low temperature (140 °C) using less expensive reagents, such as metal acetates, hexanes, thioacetamide and oleic acid. In this general route, OA was used as a fatty acid to obtain M–O complexes of cadmium, zinc and lead using their respective acetates, while thioacetamide was used to sulphurize the as obtained M–O complexes. The synthesized NCs via this generalized route were highly dispersed and stable at room temperature.

2. Experimental details

2.1. Materials

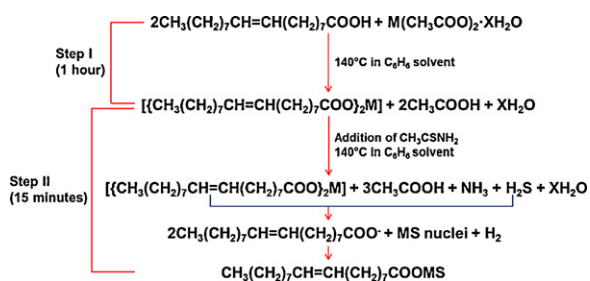
The following chemicals used in this study, cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 98.0\%$), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 98.0\%$), lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, 99.0%), thioacetamide (CH_3CSNH_2 , 99.0%), and oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, 90%), were purchased from Sigma-Aldrich, Canada. Hexanes (C_6H_{14} (mixture of isomers), 99.9%) and ethanol ($\text{C}_2\text{H}_6\text{O}$, 98%) were purchased from Fisher chemicals, Canada. All chemicals were used as received without further purification.

2.2. Synthesis of CdS, PbS and ZnS NCs

In general, O–M complexes were prepared through thermal reaction between metal acetates and OA in hexanes medium (Scheme 1). A 0.05 M of metal acetate was mixed with 0.1 M of OA and 20 ml of hexanes. The mixture was then heated at 140 °C with continuous stirring in an oil bath using water condenser. After 1 h of heating and stirring, 75 mg (~ 0.05 M) of thioacetamide were added to the hot M–O complex solution. After 15 min of additional heating and stirring, the color of the solution was changed due to the formation of metal sulphide NCs (for ZnS NCs, the solution remained transparent after sulphurization). The obtained solution was then cooled to room temperature and excess ethanol was added to precipitate the metal sulphide NCs. The NCs were centrifuged then washed many times with ethanol and hot water to remove the excess of OA and unreacted matters. The final NCs were dried in a vacuum oven at 50 °C for 2 h.

2.3. Materials characterization

TEM and selective area electron diffraction (SAED) characterizations were done using a JEOL JEM 1230 electron microscope



Scheme 1. The different steps of the possible reaction mechanism during the synthesis of OA-capped metal sulphide NCs. (i) For the two steps: M = Cd, Zn or Pb; (ii) 1st step: X = 2 for M = Cd or Zn and X = 3 for M = Pb; (iii) 2nd step: X = 0 for M = Cd or Zn and X = 1 for M = Pb.

operated at 120 kV. Samples were prepared by placing a drop of diluted colloidal solution of NCs onto a 200 mesh carbon coated copper grid. The solution was immediately evaporated at ambient temperature. The average size and size-distribution of the OA-capped CdS, ZnS and PbS NCs were also measured in solution at 25 °C and a detection angle of 90° using a Zetasizer Nano ZS90 dynamic light scattering (DLS) system equipped with a red laser (633 nm) and an Avalanche photodiode detector (quantum efficiency > 50% at 633 nm) (Malvern Instruments Ltd.). All DLS measurements were conducted with a fixed 10 runs (of 10 s each). XRD data were recorded on a Siemens D5000 X-ray diffractometer, using Cu K α radiation ($\lambda = 1.54059$ Å). Crystal size was estimated from the following Scherrer relation:

$$D = \frac{k\lambda}{B \cos \theta} \quad (1)$$

where D is the particle size, k is the shape factor (taken as 0.9), λ is the wavelength of X-ray used, β is the broadening of line at half the intensity, and θ is the diffraction angle of the line under consideration. The absorption spectra of NCs were recorded on Varian Cary 500 Scan UV–Vis spectrophotometer. The energy band gaps (E_g) of the NCs were determined from the following Tauc relation:

$$(\alpha h\nu)^2 \sim h\nu - E_g \quad (2)$$

where α (cm^{-1}) is the absorption coefficient, h (J s) is the Plank constant, ν (Hz) is the frequency of radiation, and E_g (eV) is the energy band gap of the semiconductor. Photoluminescence (PL) spectra of CdS and ZnS NCs were measured at room temperature using Varian Cary Eclipse Fluorescence Spectrophotometer (spectral range: 190–1100 nm). TGA analysis of the samples was carried out from 50 to 650 °C using a TA, Q-5000 IR instrument with a heating rate of 10 °C/min. Infrared spectra of OA and OA-capped NCs were obtained using a Nicolet (Thermo Fisher) Model 380 FTIR with an attenuated total reflectance (ATR) sampling device (model Smart Performer) with a ZnSe crystal. The infrared spectra were collected within the range of 650–4000 cm^{-1} with 10 scans per spectrum.

3. Results and discussion

As shown by the general reaction mechanism presented in Scheme 1, OA-capped metal sulphide NCs synthesis follows the following major two steps: during the first step, the hydrated metal acetate salt reacts with OA at 140 °C for 1 h in hexanes media to produce M–O complex with acetic acid and water molecules.

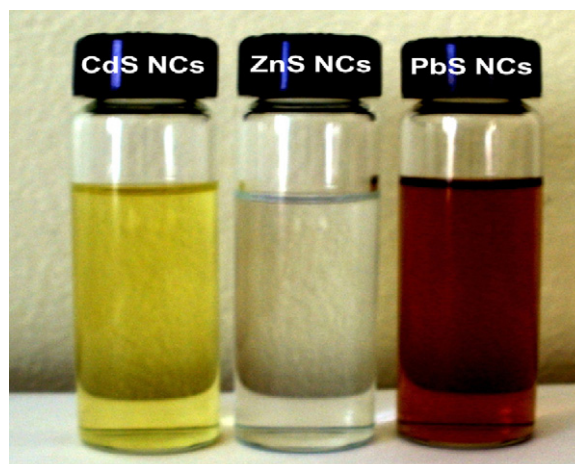


Fig. 1. Image of vials of OA-capped metal sulphide NCs.

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