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Growth kinetics and characterization of fluorescent CdS nanocrystals synthesized with different sulfur precursors in paraffin hot-matrix

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Abstract

The present paper describes the influence of the sulfur precursor on the nanocrystal growth rate and optical properties of cadmium sulfide nanocrystals in a hot-paraffin matrix. One of the precursors used is tributylphosphine sulfide; the other one is elemental sulfur. The growth kinetics is studied at various temperatures to estimate the activation energy for the formation of CdS nanocrystals from the temperature dependence of model kinetic parameters. The different sulfur precursors lead to different trends in the limiting nanocrystal radii and the time-constant of growth. The obtained nanocrystals are characterized by UV-absorption and photoluminescence spectroscopy, electrophoresis, X-ray powder diffraction and transmission electron microscopy. The nanocrystals prepared from tributylphosphine sulfide have fewer surface defects and their spectra exhibit a band-edge emission only. In this case the limiting radii of the nanocrystals increase with increasing the temperature of growth. The nanocrystals synthesized from elemental sulfur show in addition a trap-state emission due to much more surface defects. Here the limiting radii of nanocrystals decrease with increasing temperature in contrast to the previous case. In both cases, the semiconductor nanocrystals can be sterically and electrostatically stabilized in non-polar organic solvents by post-capping with tributylphosphine. Our findings are important for the controlled manufacturing of CdS nanocrystals with pre-determined properties and their utilization in a variety of optical devices.

Keywords: CdS nanocrystals; Liquid paraffin; Stearic acid; Tributylphosphine; Growth kinetics; Activation energy; Electrophoresis

1. Introduction

The colloidal semiconductor nanocrystals, called also quantum dots, are nanometer-sized polyhedron species. Being made of semiconductor materials they emit visible light under ultraviolet illumination. Unlike the bulk semiconductors, however, their emission wavelength depends on the nanocrystal diameter. Recently, fluorescent nanocrystals of CdS attract a great interest for various applications, such as biomedical labeling [1]. Starting from the first syntheses of CdS nanocrystals [2,3], they have been produced using the microemulsion method at room temperature [4]. The first synthesis of CdS nanocrystals by pyrolysis in a hot matrix (comprising tributylphosphine oxide, TOPO), is made by Murray et al. [5]. Recently Yu and Peng have developed a reproducible hot-matrix synthesis of high-quality CdS nanocrystals in octadecene solution using Cd-oleate and elemental sulfur (S) [6]. It is known that the growth conditions and the resultant photoluminescence (PL) are rather different for the hot-matrix synthesis compared to the microemulsion one.

The similarities between the microemulsion synthesis [4] and the hot-matrix synthesis are the non-polar organic solvent (matrix) with dispersed surfactant, which forms aggregates (micelles). The differences are due to the existence of a second phase (dispersed water) in the microemulsion of the w/o type, whereas in the hot-matrix the micelles are empty comprising the cadmium heads of the respective surfactant molecules [7]. Hence, in the microemulsion the cadmium ions are hydrated in the water cores of the micelles. In the hot-matrix the cadmium is connected to the anionic group of the amphiphile. The chalcogenide precursor in the microemulsion represents another water-soluble salt providing counter ions for the reaction, while it is a covalent (sulfur or selenium) compound in the hot-matrix synthesis. This difference in the precursor nature and the reaction conditions leads to different chemistry of the nanocrystal

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formation in both cases. For example, one substantial difference is the reaction temperature: it is the room temperature in the microemulsion synthesis and appreciably elevated temperature (more than 250 °C) in the hot-matrix synthesis.

The purpose of our paper is to investigate the nanocrystals growth and their PL properties in dependence of key factors such as the type of S-precursor and the temperature. In this study we use a procedure for the synthesis of CdS nanocrystals in a composite hot-matrix [7]. It utilizes liquid paraffin as a non-coordinating solvent and Cd-stearate as the precursor that is produced by stearic acid and CdO during the synthesis at once. Tributylphosphine (TBP) is used as the stabilizing ligand of the obtained nanocrystals in non-polar solvents after the synthesis.

So far only one systematic investigation has been made to study the effects of precursors on the structure and PL of nanocrystalline CdS [8]. However, this is for the preparation of CdS in aqueous solutions. In this report we represent results from studying the effects of sulfur precursor on the PL properties and growth kinetics of nanocrystalline CdS in hot paraffin matrix. Here we investigate the role of key factors (sulfur-precursor nature and temperature) for the growth of CdS nanocrystals and their effect on the optical properties. This is important, first, to realize the mechanism of the nanocrystal growth and, second, to find the most appropriate conditions (manufacturing window) for the synthesis of nanocrystals with desired properties. To complete this task, we utilize a variety of experimental methods for characterization of the nanocrystals such as TEM, XRD, electrophoresis, PL and absorbance spectroscopy. In our previous work [7] we just demonstrated the possibility to make CdS nanocrystals by the composite hot-matrix and proved the two-stage growth kinetics.

2. Experimental

2.1. Synthesis of CdS nanocrystals

In each synthesis, CdO (50 mg, 0.40 mmol) (Merck, Darmstadt, Germany), liquid paraffin (14 g) (Valerus, Sofia, Bulgaria) and stearic acid (1.00 g, 3.52 mmol) (Teokom, Sofia, Bulgaria) are put into a conical flask (25 ml in volume). Here we use smaller amount of carboxylic acid than the one described in [7], in order to obtain more monodisperse nanocrystals [6]. Then argon gas is blown trough the flask mounted on a magnetic stirrer and a flask heater. The color of the mixture solution in the flask is initially brown (due to CdO); it becomes light yellow and clear solution after heating at 150 °C (CdO and stearic acid form cadmium stearate, which is soluble in the paraffin at temperatures above 50–70 °C).

A portion of 1.5 ml (1.10 g) of the S-precursor solution (that contains 0.17 mmol of S) at a room temperature is fast injected into the hot-matrix of cadmium stearate, paraffin and stearic acid for CdS nanocrystal synthesis. The precursor molar ratio [Cd]/[S] = 2.3 is kept constant in all experiments. The swift injection of the S-precursor leads to temperature drop (that can be compensated by initial preheating) within the first few seconds after the injection. During the crystal growth in four experiments the temperature is maintained at 200 °C (473 K), 220 °C (493 K), 240 °C (513 K) or 260 °C (533 K). The uncertainty during the synthesis is ±3 K. The obtained data are averaged by three identical experiments.

Table 1
Compositions of the S-precursors

	TBP g (mol)	S, mg (mmol)	LP[a], g
S/LP	–	320 (10)	59.680
TBP-S/LP	2.22 (0.011)	320 (10)	57.460

[a] LP—liquid paraffin.

Two types of synthesis are carried out using a different sulfur precursor:

Case (i): TBP-S precursor made of sulfur dissolved in tributylphosphine (TBP) and paraffin;
Case (ii): pulverized elemental sulfur directly dissolved in the liquid paraffin.

The S-precursors are prepared by stirring at 150 °C using a reflux condenser in argon atmosphere. The amount of sulfur in each case is 0.55 wt%. The compositions of precursors are given in Table 1. The nanoparticles are isolated and purified by a procedure, described elsewhere [6,7].

2.2. Characterization

The optical properties of nanocrystal solutions (CdS is dissolved in toluene) are characterized by photoluminescence (spectrophotometer JASCO, model V-550, 100 W Hg-lamp) and absorbance spectroscopy (spectrophotometer Jenway, model 6400). High-resolution transmission electron microscopy (TEM) images of the nanocrystals are taken by using TOPCON EM 002B microscope operating at 200 kV of acceleration voltage. The sample preparation procedure for TEM is: First, the nanoparticle suspension is ultra-sonicated for good dispersion. Then a volume of the suspension is put on a copper grid, which is covered by collodion film. Finally, the excess suspension is removed by a filter paper after 30–60 s of drying.

X-ray powder diffraction (XRD) data are collected in a step-scan mode with an automatic X-ray powder diffractometer DRON-3 (Cu Kα filtered radiation, diffraction from a flat specimen, Bragg-Brentano geometry). To prepare nanocrystals for the XRD studies, the hot matrix solution is immediately dissolved in cold toluene (100 ml). After complete precipitation of the nanocrystals, the suspension is centrifuged and triple washed with the same volume of pure toluene. Then the sediment is thrice washed with a mixture of methanol and chloroform (1:1, total volume of 100 ml) [6]. Finally, starting from 150 mg CdO, about 400 mg of yellow powder that contains CdS is obtained by drying in vacuum.

The electric charge of CdS nanocrystals is evaluated by electrophoresis. The electrophoresis set-up is classical for colloidal chemistry research and consists of a high-voltage electrical supply (400 V, DC), an U-like glass tube, voltmeter and a couple of