ELSEVIER

Materials Characterization 58 (2007) 267–274

MATERIALS CHARACTERIZATION

Characterization of CdS nanoparticles during their growth in paraffin hot-matrix

Georgi G. Yordanov [a], Eiki Adachi [b], Ceco D. Dushkin [a,*]

[a] *Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria*

[b] *Advanced Research Center, Nihon l'Oreal R and D Center, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan*

Received 11 February 2006; accepted 5 May 2006

Abstract

This paper describes the optical and structural properties of CdS nanoparticles during their growth in paraffin hot-matrix containing stearic acid ligand. The nanocrystalline species are characterized with absorbance and photoluminescence spectroscopy, fluorescence microscopy, High-Resolution Transmission Electron Microscopy and X-ray diffraction. The nanoparticles size-distribution, Stokes shift and mean molar concentration are derived from the optical spectra as functions of time. Their time evolution confirms a two-stage nanocrystal growth for CdS. The stability of aggregates of stearate-coated nanoparticles, tested against UV-illumination, shows that the band-edge emission is more sensitive to photo bleaching than the trap-state emission. The obtained new quantitative results are important for the large-scale manufacturing of CdS nanoparticles and their practical applications.

Keywords: CdS nanoparticles; Liquid paraffin; Stearic acid; Tributhylphosphine; Optical properties; Size-distribution; Nanocrystal growth

1. Introduction

The chemical synthesis of semiconductor nanoparticles from ca. 1 to 20 nm in diameter is a rapidly extending area of research in materials science. In this size regime materials become to have special optical and electronic properties, which are dramatically different from those of the bulk [1–4]. Semiconductor nanoparticles of II–VI type are under intensive investigation, because of their quantum confinement [2], photocatalytic [5] and linear and non-linear optical [6] properties. Such functions find applications in photovoltaic systems [4], lasers [3], LEDs [7] and fluorescent biological labels [8].

For the production of monodisperse in size nanoparticles of CdX (X=chalcogenide) a hot-matrix method is used. Its first variant applies TOPO (trioctylphosphine oxide) as high-boiling solvent (matrix) and organometallic precursors like dimethyl cadmium [9]. Later research showed that the organometallic precursor could be successfully replaced by CdO [10] or by cadmium acetate [11,12] for preparation of CdS, CdSe or CdTe nanoparticles. Recent studies replace TOPO with non-toxic solvents like octadecene [13] or liquid paraffin [12].

The quantum confinement effect, usually manifested as peculiarities in the optical spectra, and the ease of their synthesis, developed by us, makes the CdS nanoparticles

* Corresponding author. Tel.: +359 2 8161 387; fax: +359 2 962 5438.
E-mail address: nhtd@wmail.chem.uni-sofia.bg (C.D. Dushkin).

1044-5803/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.matchar.2006.05.010

attractive for the practice. The purpose of this paper is to reveal the changes in the optical properties of nanocrystalline CdS during its growth in a paraffin hot-matrix, which are not systematically investigated so far. In order to describe the so-called "focusing of size distribution" in this case [14], we adopt known analytical solutions [15] for the variance of size distribution calculated from the optical spectra. The same strategy has been successfully applied for studying of the size-focusing phenomenon for CdSe nanoparticles synthesized in TOPO hot-matrix [15]. The mean molar particle concentration can be calculated from the optical spectra as previously described [16]. Here we apply the same procedure to trace the temporal evolution of the CdS particle concentration during the growth process. The photo bleaching of CdS nanoparticles, prepared in hot paraffin media, is also investigated.

The new quantitative results obtained by us can serve as the guidance for manufacturing of CdS nanoparticles and their practical utilization.

2. Experimental section

2.1. Nanocrystal synthesis

Three syntheses are carried out at 250 °C in order to check the reproducibility of the nanocrystal growth. In each of them 50 mg (0.40 mmol) of CdO (Merck, Germany), 9.00 g of liquid paraffin (Valerus, Bulgaria) and 1.00 g (3.52 mmol) of stearic acid (Valerus, Bulgaria) are put together in a conical flask (50 ml). The mixture becomes transparent after heating at a temperature higher than 150 °C. The sulfur solution is prepared from 166 mg elemental sulfur and 30.00 g paraffin and heated to 50 °C prior to the injection. Then 1.7 g (~2.0 ml) of 0.55-wt.% sulfur solution, equivalent to 0.28 mmol of sulfur, is fast injected in the flask at 280 °C. After the initial temperature drop due to the injection, the temperature is fast adjusted at 250 °C and kept constant throughout the entire synthesis.

Although we follow the synthesis procedure of CdS nanoparticles described elsewhere [12], here the amount of stearic acid is reduced twice than the reported one in order to obtain more monodisperse in size nanocrystals. This expectation is in accord with the data from similar synthesis of CdS nanocrystals in octadecene solution [13] where reducing the amount of the acidic ligand (oleic acid) leads to nanocrystals of narrower size distribution. Here the molar ratio of precursors in the system, [Cd]/[S], is about 1.4.

Preliminary experiments showed that the growth rate and the nanoparticle radius do not significantly depend on the stirring rate of the reaction solution (the deviations are within the experimental error).

2.2. Aliquot sampling

Aliquots are taken at different time intervals. An aliquot (~0.1 ml) is fast injected into 1.00 g of 5-wt.% tributhylphosphine (TBP) solution in toluene (TBP is purchased from Aldrich). TBP dissolves unconsumed Cd (II) stearate. The weight of aliquot is determined by subtracting the mass of the TBP/toluene solution from the total mass of the TBP/toluene solution plus reaction aliquot. Then the sample concentration is adjusted by adding toluene to each sample in order to be 0.0500 g of the aliquot in 2.00 g of TBP/toluene solution. This adjustment is for accurate comparison of the exciton absorbance intensity. From here one can obtain a precise value for the mean nanoparticle concentration (see below). The time for each sampling is 1-2 s, which can be considered as the uncertainty of time measuring. Each sample is then analyzed at a room temperature by fluorescence and UV–vis absorbance spectroscopy (spectrophotometer Jenway, model 6400).

2.3. Purification and characterization

The nanoparticles are purified from the paraffin and stearic acid in the following way. The hot reaction solution (~250 °C) is fast poured into 100 ml of cold toluene 40 s after completion of the CdS nanoparticle growth. Then the obtained precipitate is centrifuged and washed twice with pure toluene and twice more with pure n-heptane. The obtained new precipitate contains stearate-coated CdS nanocrystals, which fluoresce under UV-illumination (365 nm). The excess Cd(II) stearate is removed by washing the precipitate with methanol as described elsewhere [13]. Absorption and photoluminescence (PL) spectra of the purified nanoparticles are also measured.

The stearate-coated CdS nanoparticles are visualized using a fluorescent microscope (Leica DMRB, 10×–40× objective lenses, long pass filter 425 nm). The stability against photo bleaching is tested under UV-illumination (100 W Hg lamp, band pass filter 340–360 nm). The emission longer than 425 nm is detected by a linear CCD spectrometer (USB2000, Optosirius, 350–850 nm) attached to the microscope.

The nanoparticles are visualized by High-Resolution Transmission Electron Microscopy, HR-TEM (TOPCON EM 002B microscope, acceleration voltage 200 kV). They are also characterized by X-ray powder diffraction (XRD) in a step-scan mode with an automatic X-Ray powder diffractometer (DRON-3, Cu K-alpha filtered radiation, diffraction from a flat specimen, Bragg–Brentano geometry).