The effects of temperature and carboxylic acid ligand on the growth of nanocrystalline CdSe in a hot paraffin matrix

Georgi G. Yordanov [a], Gospodinka D. Gicheva [a], Bocho H. Bochev [a],
Ceco D. Dushkin [a,*], Eiki Adachi [b]

[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&D Center, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan*

Abstract

This paper describes the temperature and the ligand type dependence of the growth kinetics of CdSe nanoparticles synthesized by a version of the hot-matrix method. In this method the composite matrix comprises a non-coordinating solvent (liquid paraffin) and a coordinating ligand (carboxylic acid). As a Cd-precursor serves cadmium carboxylate in situ obtained from CdO and an excess amount of carboxylic acid (stearic or oleic one). The Se-precursor is tributhylphosphine selenide prepared from Se powder and tributhylphosphine (TBP) in the liquid paraffin. The temperature and the carboxylic acid type are varied maintaining constant the precursor amount and the concentration of carboxylic acid in all experiments. It is found that the radius of initial nuclei, the limiting radii of fast and slow growth and the time-constant of the fast growth depend on the temperature and the fatty acid type. The temperature dependence of the rate constant of fast (reaction limited) growth is Arrhenius type. We suppose that the observed difference in the kinetics of growth in the presence of stearic or oleic acid is due to the existence of a double bond in the oleic acid molecule on the particle surface. It leads to steric hindrance between the Cd-oleic monomer and the subsurface layer around the growing nanoparticle.
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1. Introduction

The colloidal semiconductor nanocrystals, known also as quantum dots, are nanometer-sized, single crystalline fragments of the corresponding bulk crystals, which have well-controlled size and size distribution and are dispersible in various solvents or other media. Recently, semiconductor nanocrystals attract a great interest in both fundamental research and applications, such as LEDs [1], lasers [2], solar cells [3], and biomedical labelling [4,5]. As the most utilized system in terms of synthesis, high-quality CdSe nanocrystals with nearly monodisperse size and shape are in active industrial development for labelling reagents [6–8]. The best suitable method for the synthesis of semiconductor nanocrystals is the pyrolysis of cadmium and selenium precursors in a hot amphiphilic matrix originally cre-

ated in Refs. [9,10] (for a review see Ref. [11]). Peng and Peng [12] have first developed a reproducible hot-matrix synthesis of high-quality CdSe nanoparticles using CdO as cadmium precursor. This allowed avoiding of the organocadmium precursor dimethyl cadmium typical for the classical hot-matrix synthesis [9–11] and paved the ways for new synthetic routes.

In this study we demonstrate a version of the hot-matrix method for the synthesis of CdSe nanoparticles using liquid paraffin as the matrix (non-coordinating solvent) and carboxylic acid (stearic or oleic one) as the coordinating ligand. Tributylphosphine (TBP) is applied as the stabilizing agent, complementary to the ligand. As a whole, the temperature in our synthesis (190–280 °C) is much less than that in the classical synthesis using trioctylphosphine oxide, TOPO (300–350 °C). CdSe nanocrystals can finally be isolated and used for further investigation or chemical surface modification.

The purpose of our paper is to investigate the effects of key parameters such as the temperature and the ligand type on the

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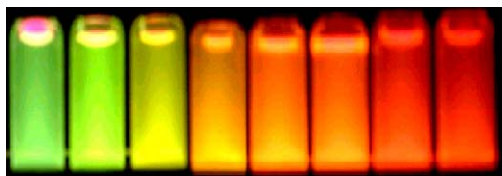*E-mail address:* nhtd@wmail.chem.uni-sofia.bg (C.D. Dushkin).

Fig. 1. Photoluminescence of CdSe nanoparticles with different diameters in heptane; from left to right the nanoparticle size is increasing. The diameter of one glass tube is c.a. 1 cm.

growth kinetics of CdSe nanocrystals in the new matrix comprising liquid paraffin and a carboxylic acid ligand. This necessarily leads to a comparison with the growth conditions in the classical TOPO matrix.

To study the growth of nanocrystals in the composite hot-matrix we follow the size-dependent optical properties of the nanocrystals (Figs. 1 and 2). It is found that the nanoparticle radius, calculated from the absorbance spectra (Fig. 2a) and plotted versus time at different temperatures and ligands, increases via two processes: fast and slow ones, which are very similar to those for CdSe nanoparticles in the TOPO matrix [11]. The sharp increase of the radius at the beginning of nanoparticle growth (fast process) is due to a reaction-driven growth during which the precursor from the nanocrystal vicinity adsorbs on its surface crossing the capping layer of surfactant molecules there. It exhausts the subsurface layer, adjacent to the nanoparticle surface, from material, which leads in turn to sharpening of the nanoparticle size distribution known as focusing [13]. The subsequent plateau-like process (slow process) is a diffusion-limited growth, when the precursor moves from distinct parts of the suspension to the subsurface layer.

The model parameters extracted from the experimental data are of a reasonable magnitude and appearance. The limiting radii of reaction and diffusion growths linearly increase with the temperature. The average radius of the initial nuclei also increases with the temperature with its values for oleic acid being larger than those for stearic acid. The time constant for the reaction-driven growth decreases with the temperature, which is due to the Arrhenius-like temperature dependence of the rate constant of growth.

Our results demonstrate the possibility to replace the classical TOPO matrix with the new composite matrix, which has many advantages such as lower synthesis temperature, much lower price and environmental suitability. We outline also the control of the growth of high quality CdSe nanoparticles (shining brightly in Fig. 1) by varying the temperature and the ligand type.

2. Experimental section

2.1. Synthesis of CdSe nanoparticles in liquid paraffin and characterization

Three materials, 50 mg of CdO (Merck), 15 ml of liquid paraffin (Valerus, Sofia) and 2 g of stearic acid (Teokom, Sofia) or oleic acid (Valerus), are put in a conical flask (25 ml in volume). Then argon gas is blown trough the flask in a silicon oil bath on a magnetic stirrer and a flask heater. Though the color of the mixture solution in the flask is initially brown, it becomes colorless and transparent solution after heating at 150 °C. Most probably, CdO and stearic acid form cadmium stearate in the hot solution (respectively, cadmium oleate with oleic acid). Meanwhile 100 mg of Se powder is dissolved in 10 ml of liquid paraffin and 0.5 ml tributhylphosphine (Merck) at 150–200 °C using a reflux condenser in argon atmosphere. This also becomes colorless and transparent solution after heating at 150–200 °C. A 2.5 ml portion of the hot TBP-Se solution is fast injected into the hot-matrix of cadmium carboxylate, paraffin and carboxylic acid. (The reactor temperature is set almost 15 °C higher than the growth temperature to compensate the temperature drop within the first few seconds after the swift injection of the Se solution.) The mixing makes the colorless solution yellow, which subsequently changes to red. Samples are collected from the reaction mixture at given time intervals for evaluation of the particle growth kinetics. The rate of nanocrystal growth has been determined at four different temperatures using either stearic or oleic acid as the coordinating ligand.

To measure the nanoparticle absorbance, a portion of 0.4 ml of each collected sample is diluted in 2.5 ml of *n*-hexane (or toluene) and 1–2 drops of TBP are added. Each sample is well agitated using a 15 kHz ultrasonic bath for about 5 min. The absorbance spectra of the nanoparticle suspensions stabilized with TBP are measured at room temperature with spectrophotometer Jenway (model 6400). The red shift of their peaks with the time is implying on the growth of nanoparticles (Fig. 2a). Similar shift is observed also with respect to the
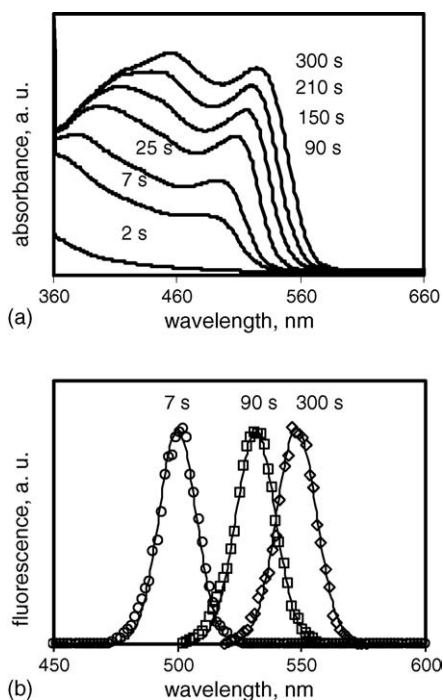

Fig. 2. Typical temporal evolution of (a) absorption and (b) emission spectra of CdSe nanocrystals grown at 190 °C in oleic acid/paraffin matrix. The time (s) when each sample is taken is shown with numbers on the figure. The photoluminescence spectra are represented as data points, measured experimentally, and solid lines simulated as Gaussian fits.