Monodisperse CdSe Nanorods at Low Temperatures

Thomas Nann* and Jürgen Riegler[a]

Abstract: A new synthetic method is presented that allows the preparation of highly monodisperse CdSe nanorods (so called quantum rods) at relatively low temperatures (160 °C). This method is characterized by a high aspect ratio of the particles and affords good reproducibility. The morphology of the resulting nanorods was examined by means of transmission electron microscopy (TEM) and the electro-optic properties by means of fluorescence spectroscopy. The conditions of the reaction of nanoparticle growth were examined by varying the concentration of the organometallic precursors, the growth temperature, and the growth time. The experimental findings correspond well with previously published semiempirical pseudo-potential calculations.

Keywords: materials science · nanotechnology · quantum rods · semiconductor nanoparticles · synthetic methods

Introduction

In the last decade, semiconductor nanoparticles have been of increasing interest in many disciplines of science. Essentially, three reasons are responsible: first, a quantum size effect can be observed in semiconductor nanoparticles because of the quantum confinement, which has been predicted for a long time; second, highly monodisperse nanoparticles have been available since the early nineties; and third, this new class of materials has an extraordinarily high potential for applications, particularly as labels for biological molecules,[1] as phosphors,[2] in polymer–LED applications,[3] in polymer electronics,[4] and in photovoltaic devices.[5]

Initially, science was focused on quantum dots, which can be prepared in a highly monodisperse form under mild conditions.[6] The electronic structure of quantum dots has been described extensively in theory[7] and has been verified by many scientists.[8]

The synthesis and characterization of quantum rods (QRs) has already been reported.[9] The present paper reports a new synthetic route enabled by a new starting precursor (cadmium naphthenate). In contrast to the previous studies, the new method is performed at much lower temperatures and in a different reaction medium.

Even before it was possible to prepare monodisperse QRs, changes in the electronic structure due to the elongation of the crystallographic *c* axis could be expected. Furthermore, it has been shown that QRs exhibit a polarized photoluminescence.[10] These properties lead to many new and potentially interesting electro-optic applications, such as the development of materials with anisotropic macroscopic properties.

Results and Discussion

The newly developed CdSe quantum rod synthesis has been investigated in terms of its kinetic and thermodynamic reaction parameters. Concentration, temperature, and time were each varied, while keeping the remaining two parameters constant. The morphology of the particles was measured by means of transmission electron microscopy (TEM). It was observed that rods with a high aspect ratio at nucleation were formed.

With relative ease and under mild conditions, QRs were obtained that show polarized photoluminescence in the complete wavelength range achieved by quantum dots. The half width of the peaks in the emission spectra was usually about 35 nm. The results are presented in detail below.

Transmission electron microscopy (TEM): Quantum rods of varying thickness were examined and measured by means of TEM. Figure 1a–e present QRs with diameters of approximately 2.0, 2.4, 3.1, 3.8, and 4.6 nm, respectively. The measurements were taken from TEM micrographs and exhibit an average standard deviation of 10%, whereby this does not necessarily correspond to the thickness distribution of the QRs. The lengths of the rods vary from about 10 to 20 nm. Typical aspect ratios of approximately 3.5 were measured for all samples. Due to the quantum confinement, these rods show luminescence in colors ranging from blue to red (see Figure 2).

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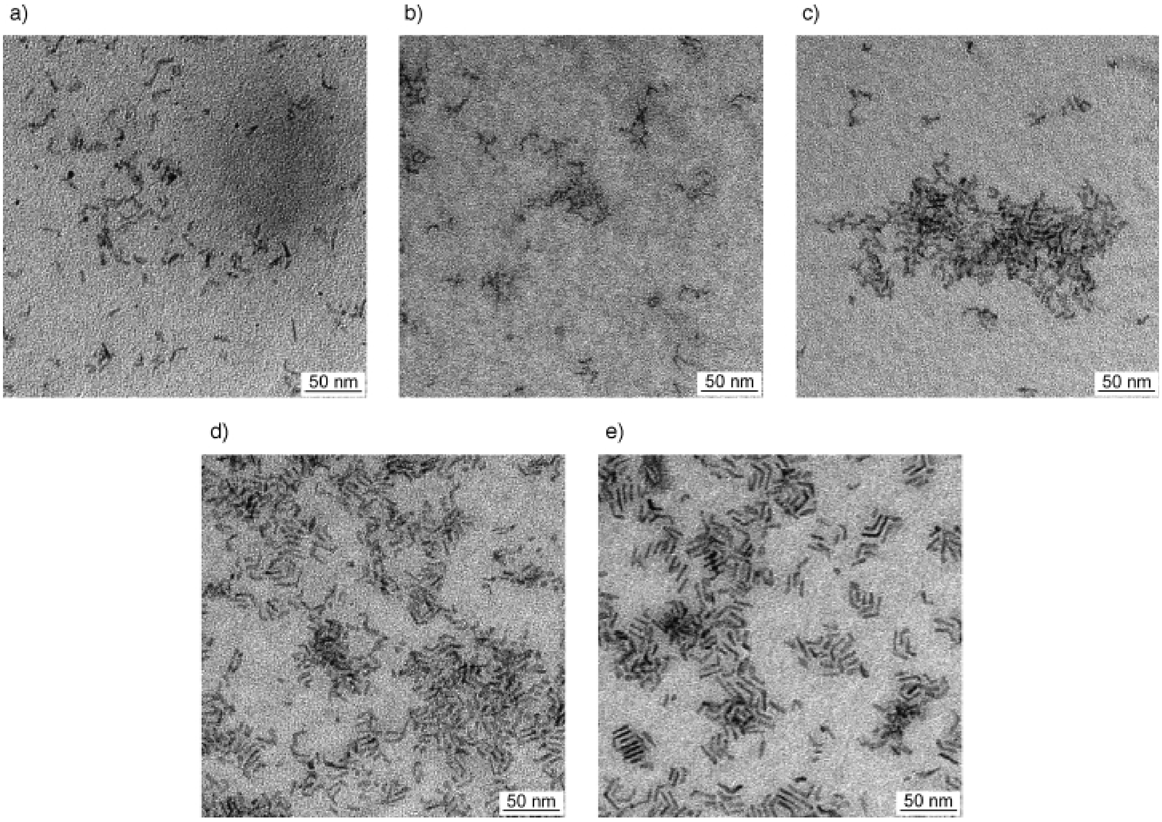

Figure 1. TEM micrograph of CdSe nanorods grown at a) 160 °C, b) 180 °C, c) 200 °C, d) 220 °C and e) 240 °C for 5 minutes.

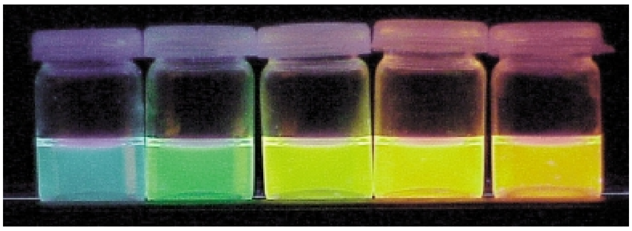

Figure 2. Photographic image of CdSe nanorod colloids in chloroform (from left to right ca. 2.0, 2.4, 3.1, 3.8, and 4.6 nm). The photoluminescense was excited with an UV lamp at 366 nm.

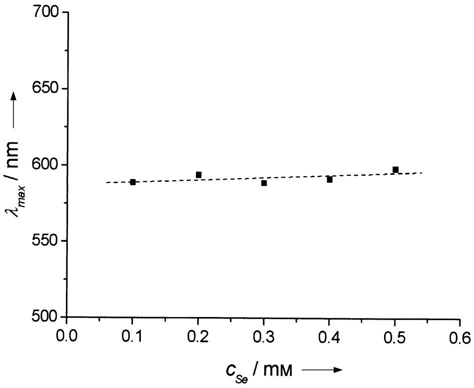

Figure 3. Fluorescence emission maxima versus concentration of the precursors in the reaction flask. Ratio cadmium:selenium 1.2:1 in all experiments.

TEM measurements indicate that some of the quantum rods are bent. The angle of this bend was measured, and it was observed to be 112° for all bent rods. The "bent" QRs appear to be twins with the angle corresponding to the distorted tetrahedron of the wurtzite lattice.

Concentration dependency: We investigated the influence of the variation of concentration of the organometallic precursors (i.e., cadmium naphthenate and Se/trioctylphosphine (Se/TOP)) on the growth rate of the nanocrystals. Temperature and reaction time were kept constant for all experiments. The Se/TOP solution was injected at 250 °C with a particle growth time of five minutes at 220 °C. Figure 3 shows the interdependence of the emission maximum λ_{max} of the nanoparticles formed and the concentration of the selenium injected. For all concentrations, particles with an emission maximum of about 590 nm were found. Also, the half width of the peaks in the emission spectra differed only slightly (about 35 nm).

This means that controlling the growth of the particles is much easier as the concentration has no influence on the chemical kinetics and a linear scale-up is performed easily within the concentration range measured.

Temperature dependency: To investigate the dependency of the growth rate on the temperature, the concentration of the organometallic precursors and the growth time was kept constant: all syntheses were performed at a Se/TOP concentration of 300 μmol in hexadecylamine (HDA; 4 g) within a period of five minutes. As stated in a previously published synthesis for CdSe nanoparticles (quantum dots),[11] no influence of the injection temperature on the nucleation and particle growth was observed for the new synthesis in HDA. Nevertheless an injection temperature above growth temperature was chosen to prevent a temperature decline below the growth temperature due to mixing the cold Se/TOP solution with the hot HDA solution.

Growth temperatures of between 140 °C to 240 °C were investigated. Under these conditions, nanorods with emission maxima of between about 500 nm and up to more than 600 nm are formed. This corresponds completely with the photoluminescence (PL) achieved for CdSe quantum dots. Figure 4 shows the PL emission spectra of the nanoparticles formed at the various growth temperatures. Figure 2 shows dispersions of these particles in chloroform excited to luminescence at 366 nm by means of an ultraviolet lamp. Figures 2 and 4 demonstrate the high uniformity of the nanoparticles formed (typical half width maxima of 35 nm).

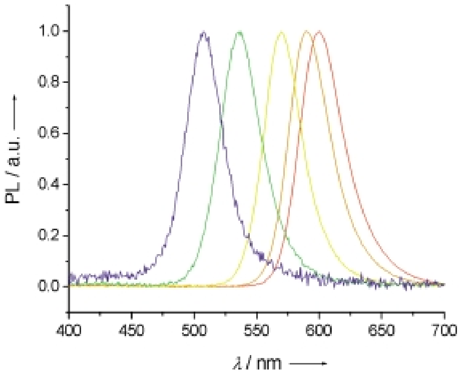

Figure 4. Fluorescence spectra of CdSe nanorods in chloroform. The spectra were recorded from the particles depicted in Figure 1a – e (from left to right).

Figure 5 shows emission maxima plotted against the various growth temperatures. A linear correlation can be observed between growth temperature and emission maxima for temperatures below 200 °C. No linear correlation could be found for temperatures above 200 °C. For temperatures below 160 °C, no luminescent particles could be found within the growth times investigated (5 min.).

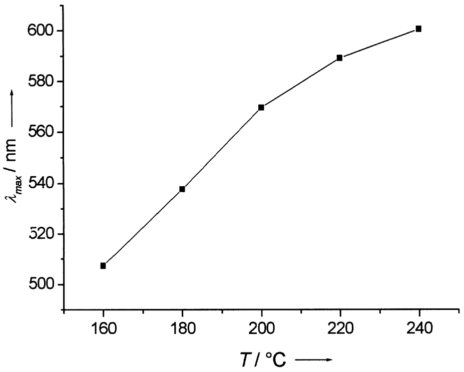

Figure 5. Growth temperatures of CdSe nanorods versus photoluminescence maximum ($\lambda_{\max}$). All particles were grown for 5 minutes.

The high reproducibility of the dependency of the PL emission maximum (and the growth rate) of the particles from the growth temperature can intentionally be used to create rods of a defined diameter. Because growth temperature and growth time can be easily controlled and as it has already been determined that the concentrations of the organometallic precursors have no influence on the particle growth, we were able to synthesize nanoparticles of given emission maxima to within a nanometer.

The volumes of the synthesized nanorods were determined by means of TEM. In addition, the concentration of Cd from the reaction supernantant was determined by means of atomic absorption spectroscopy (AAS). The number of particles formed (and the yield) can be calculated from the volume of the particles and the concentration measured. The results of these measurements and the calculations are given in Table 1. It was observed that more particles formed at low growth temperatures rather than at higher temperatures.

Table 1. Results of CdSe nanorod growth in HDA at different temperatures.

growing temperature [°C]	$\lambda_{\max}$ [nm]	rod width [nm]	number of particles [nmol]
240	600.6	4.61	40.5
220	589.2	3.85	55.4
200	569.6	3.13	68.5
180	537.7	2.44	104.1
160	507.4	2.00	186.2
140	–	–	–

Time dependency: The last parameter investigated was the time of particle growth. For this, the concentrations of the organometallic precursors and the temperature were kept constant. By means of a special reaction arrangement, fluorescence emission spectra were taken in situ during the course of the reaction. The concentrations of the precursors were 360 μmol of cadmium naphthenate in HDA (4 g) and 300 μmol selenium in TOP. The measurements were taken at 160 °C. The experiment was terminated after three hours. Figure 6 shows the temporal course of the fluorescence emission maxima. As can be seen, the width growth of the nanorods takes a logarithmic course. Figures 5 and 6 reveal that the reaction kinetic follows a broken reaction order.

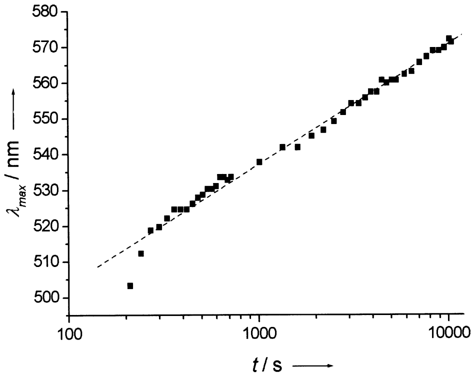

Figure 6. Photoluminescence maxima ($\lambda_{\max}$) of CdSe nanorods versus growth time. Spectra were recorded in situ at a growth temperature of 160 °C.

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These results suggest the possibility of controlling the size of the nanoparticles through the growth time. Because the particles grow slowly, the reaction can easily be terminated at the desired particle size.

By comparing the spectra of both the reaction start and end, we observed that the half width of the peaks in the emission spectra drops from about 50 nm to 30 nm. This leads to the conclusion that slow particle growth leads to increased monodispersity. This also allows for the increase of monodispersity of the particles by slow growth at low temperatures and the termination of the reaction at a desired wavelength.

Theory: By pyrolysis, Li et al. prepared CdSe quantum rods of various widths and lengths from dimethyl cadmium and Se/tributylphosphine in a mixture of trioctylphosphine oxide (TOPO) and hexylphosphonic acid (HPA).[12] They investigated the correlation between the effective band-gap energies of the QRs and the length and width of the rods. They found that the effective band-gap energy depends on both the width and the length of the nanorods. It was observed that the photoluminescence of the QRs prepared by the new method seems to depend solely on the width of the rods and not on the length. Because the QRs formed by the new method show an aspect ratio of mostly over 3.5 and the rods prepared by Li et al. a minor aspect ratio, this finding corresponds well to the quantum mechanical calculations.[13] Additionally, the fact that the QRs show a red shift of the photoluminescence relative to quantum dots of the same diameter corresponds to theoretical expectations.[14]

The effective band-gap energies of the nanorods were calculated from the emission maxima; the radii were taken directly from the TEM measurements. Figure 7 depicts a plot of these values. Fitting with $1/r$ leads to a good correlation, but it must be stressed that this correlation is found empirically and depends, according to the theory, also on the aspect ratio of the nanorods.

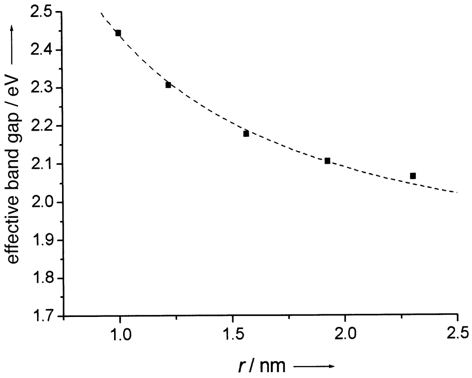

Figure 7. Effective band gaps (calculated from photoluminescence maxima) of CdSe nanorods versus width of the particles (estimated from TEM micrographs).

Conclusion

A new synthesis method is presented here that allows the preparation of quantum rods with a high aspect ratio. The new method is easily reproducible and can be performed under mild reaction conditions. Furthermore, the reactants are readily available and, with respect to their toxicity and risk, uncomplicated. It was demonstrated that the reaction could be controlled by variation of the growth temperature and the growth time. For the first time, a method has been presented that allows nanoparticle synthesis on an industrial scale. The low reaction temperature allows a synthesis with usual reaction apparatus because the temperatures is always below 260 °C, which is the softening point of most PTFE sealings and components.

Experimental Section

Transmission electron microscopy (TEM) measurements were carried out on a LEO 912 Omega operating at 120 kV. Fluorescence spectroscopy was executed on a J&M FL3095 fluorimeter. Atomic absorption spectrometer (AAS) measurements were performed on a Analytik Jena AG, model AAS vario 6 spectrometer. Cadmium naphthenate was purchased form Alfa Aesar (Karlsruhe, Germany), all other chemicals from Aldrich (Munich, Germany).

A typical CdSe nanorod synthesis was carried out by dissolving cadmium naphthenate (17.2 % Cd, 235.3 mg, 360 μmol) under inert gas atmosphere (N_2) in hexadecylamine (4 g) within a Schlenk flask. The solution was heated to 190 °C and degassed three times. A solution of selenium (23.7 mg, 300 μmol) in trioctylphosphine (2 mL) was prepared in a drybox and transferred into a syringe. The selenium solution was quickly injected into the cadmium solution under Schlenk conditions, and the mixture was stirred for 5 minutes at 160 °C. The reaction mixture was allowed to cool down to room temperature, and the nanorods were precipitated with dry methanol. After centrifugation, the cadmium concentration was measured in the supernatant. The yield was calculated to 51 % (29.3 mg, 0.186 μmol) nanorods with approximately 2 nm width and 10 nm lengths. The nanorods were washed three times with dry methanol and redissolved in chloroform for further measurements.

Acknowledgements

The authors thank Dr. R. Thomann for help with the TEM measurements, and S. Hirth-Walther for assistance with the AAS measurements.

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Received: May 3, 2002 [F4064]