Colloid Polym Sci (2005) 284: 229–232
DOI 10.1007/s00396-005-1370-x

SHORT COMMUNICATION

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Synthesis of high-quality semiconductor nanoparticles in a composite hot-matrix

Received: 23 December 2004
Accepted: 9 June 2005

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Abstract Semiconductor nanocrystals are of a great interest for many practical applications which motivates the search of low cost and environmental-friendly methods for their manufacturing. Here we report the synthesis of CdSe and CdS nanoparticles utilizing composite matrix of liquid paraffin as a non-coordinating solvent and stearic acid as a coordinating ligand. The nanoparticle growth kinetics is compared to that of the classical synthesis in trioctylphosphine oxide matrix. It is found that the nucleation and crystal growth are remarkably affected by the coordinating ligand. The CdSe and CdS nanocrystals can be isolated and purified from the matrix which makes it possible their large-scale synthesis for applications.

Keywords CdSe nanocrystals · CdS nanocrystals · Liquid paraffin matrix · Stearic acid · Nanoparticle growth kinetics

Introduction

Semiconductor nanoparticles (quantum dots, QDs) are applied in photovoltaics, LEDs and lasers, diagnostic labels in medicine, etc. They require an increasing amount of high-quality nanoparticles synthesized by cost-effective and environmental-friendly methods. In the previous hot-matrix methods [1, 2] an organometallic precursor, e.g., dimethyl cadmium, is employed for the preparation of semiconductor nanoparticles. However, the organometallic precursors are expensive, difficult for synthesis and very toxic. The usage of CdO as Cd precursor [3] in a molten coordinating matrix of trioctylphosphine oxide (TOPO) is the most preferred way, because of nonuse of organometallics. However, the use of such coordinating matrixes is restrictive for the large-scale production of nanoparticles, because of expensive regeneration cost of the matrix and environmental pollution at disposal. Although there are suitable liquids and surfactants for the low-temperature microemulsion synthesis [4], the monodispersity of nanoparticles is rather low. In this study we report a modified procedure for the synthesis of $A^{II} B^{VI}$ type semiconductor nanoparticles by a non-coordinating matrix of liquid paraffin and stearic acid as a coordinating ligand. A procedure, using octadecene and oleic acid is known from the literature [5]. In our case we have chosen the couple liquid paraffin (matrix solvent) and stearic acid (ligand), because they are low-cost and environmental-friendly materials. Moreover, we obtain high-quality CdSe and CdS nanoparticles using this method. Furthermore, we compared the two kinetics of their growth at 250 °C in liquid paraffin and in TOPO in order to evaluate both matrices.

Experimental procedure and results

Three materials, 50 mg (0.38 mmol) of CdO, 15 ml of liquid paraffin and 2 g (7.0 mmol) of stearic acid, are put in a Schlenk flask (50 ml in volume). Then argon gas is blown through the flask mounted on a silicon oil bath on a magnetic stirrer and a flask heater (argon is not absolutely necessary prerequisite). Though the color of the solution mixture in the flask is initially brown, it becomes transparent (or slightly yellowish) clear solution after heating at 250 °C. Meanwhile 100 mg (1.26 mmol) of Se is dissolved in 10 ml of liquid paraffin and 0.5 ml (2.0 mmol) tributhylphosphine (TBP) at 150–200 °C using reflux condenser in argon atmosphere. This also becomes transparent clear solution after heating at 150–200 °C. A portion of 2.5 ml of the hot TBP-Se solution is fast-injected into the hot-matrix of CdO, paraffin and stearic acid. The mixing makes the transparent solution yellow which subsequently changes to red. Samples are taken from the reaction mixture at given time intervals for evaluation of the particle growth [6, 7]. In another experiment, the reaction mixture is immediately cooled down for isolation of CdSe nanoparticles at a desired size.

In the comparative experiments, TOPO (15 g, 38.8 mmol) is used as a matrix solvent instead of liquid paraffin. It is found that cadmium acetate $Cd(OAc)_2$ can also serve as a cadmium precursor in non-coordinating solvents such as liquid paraffin. In this case, 100 mg (0.37 mmol) of $Cd(OAc)_2$ dihydrate are used instead of CdO.

The CdSe nanoparticles are purified from the matrix by the following way. A portion of 5 g of the cooled matrix is dissolved in 100 ml of *n*-hexane using an ultrasonic bath for 5–10 min. The solution is centrifuged for 5–10 min at 4,000 rpm with a rotor (10 cm in radius). The sediment is washed with *n*-hexane twice for better purification. The fluorescence of the particles remains the same when dispersed in different nonpolar solvents: *n*-hexane, *n*-heptane, paraffin, toluene, etc. (at equal particle concentrations). For better purification, an extraction of the above dispersions with methanol can be made.

The growth kinetics of the nanoparticles is traced by measuring the absorbance and the fluorescence of the samples, collected from the hot-matrix at time intervals 15, 30, 60, 180, 300, and 480 s after the beginning of growth. A portion of 0.4 ml of each sample is diluted in 2.5 ml of *n*-hexane and 2–3 drops of TBP are added. Each sample is well agitated using a 15 kHz ultrasonic bath for about 5 min. After these procedures the absorbance and fluorescence spectra are measured. Figure 1a shows the absorbance spectra at given time intervals. The temporal evolution of the PL-maximum is shown in Fig. 1b. In both cases their peaks shift to larger wavelengths with the time implying on the growth of nanoparticles [6, 7].

CdS nanoparticles are synthesized and evaluated in a similar way. In this case sulfur is used instead of selenium. The solution of tributylphosphine sulfide (TBP-S) is made by dissolving of 210 mg sulfur into 50 ml of liquid paraffin and 2.5 ml of TBP. This TBP-S is further used instead of TBP-Se in the synthesis. Figure 2 shows the respective absorbance and PL-spectra of two samples taken from the matrix at time intervals 35 and 55 s after the beginning of nanoparticle growth. Similarly the shifts toward larger wavelengths are observed, which indicates nanoparticle growth. It is found that instead of TBP-S, a solution of sulfur in liquid paraffin (4.2 mg/ml) could also be applied as a precursor.

In Fig. 3 are shown TEM images of the stearic acid capped QDs. The rather regular spacing between the inorganic QDs is probably an evidence of the presence of a capping layer around them.

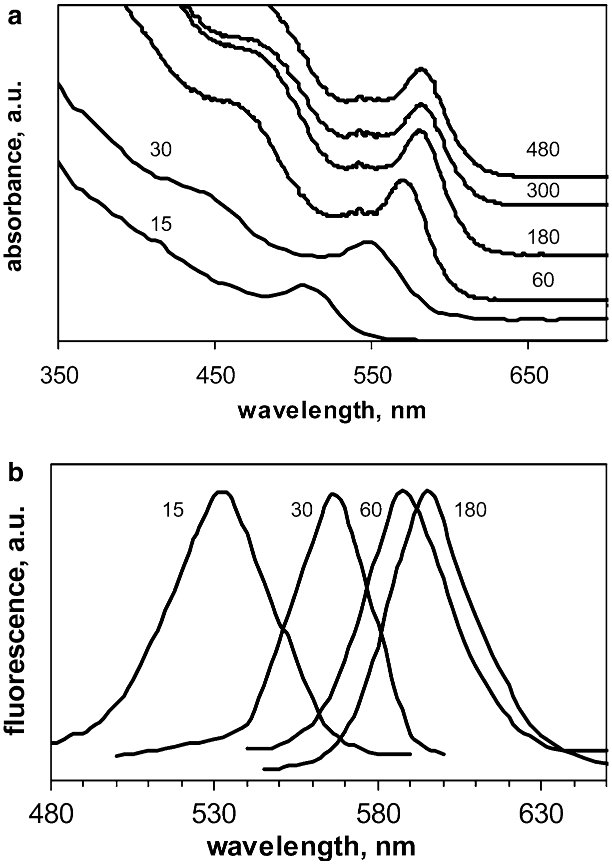

Fig. 1 Temporal evolution of the absorbance (**a**) and photoluminescence (**b**) spectra of CdSe nanocrystals, prepared at 250 °C in liquid paraffin matrix using CdO precursor. The time after beginning of nanocrystals growth (in seconds) is shown with *numbers on the lines*. Spectra are taken in hexane solutions at a room temperature

Discussion

In order to compare the two matrices, coordinating (TOPO) and non-coordinating (liquid paraffin), two experiments have been made. The reaction temperature, the precursor concentrations and the concentration of stearic acid are the same except use of TOPO instead of use of liquid paraffin. The nanoparticle size throughout the growth is calculated from the optical spectra in Fig. 1a using the equations derived in [7]. The calculated radii of nanoparticles are plotted in Fig. 4 in the case of CdSe. As seen, they are composed of two growth kinetics—fast and slow, which is very similar to that observed with CdSe nanoparticles in pure TOPO matrix [7]. The fast increase of the radius at the beginning of nanoparticle growth is due to a reaction-driven process during which the precursor from the nanocrystal vicinity adsorbs on its surface crossing the capping layer of surfactant molecules there. This process exhausts the subsurface layer, adjacent to the nanoparticle surface, from material, which leads to sharpening of the nanoparticle size distribution known as focusing [6]. The subsequent slow process at large times is a diffusion-limited growth, when the precursor moves from distinct parts of the suspension to the subsurface layer. Quantitatively, this kinetics is described by the set of equations, outlined in [7]—see Eq. 33 for the fast growth and Eq. 34 for the slow one. Table 1 summarizes the values of fitting parameters used in the calculations for the two matrices.

Further growth of the nanocrystals can be due to Ostvald ripening—this is the "defocusing of size distribution" and should be avoided for the formation of relatively monodisperse colloidal nanocrystals.

The results in Fig. 4 and Table 1 show that the nucleation and growth processes are slower when TOPO is used. Also, smaller nanocrystals are obtained in the TOPO matrix. In both cases, the Cd-monomer is Cd-stearate that is formed in situ by heating the CdO and stearic acid. However, the fatty acid is found to be absolutely necessary for the growth of nanocrystals in the non-coordinating solvent (paraffin). To prove this fact more experiments are made in liquid paraffin and

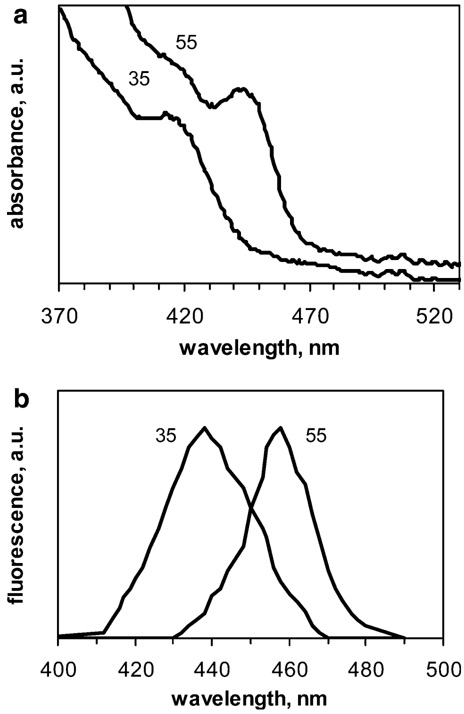

Fig. 2 Temporal evolution of the absorbance (**a**) and photoluminescence (**b**) spectra of CdS nanocrystals, prepared by using TBP-S/paraffin precursor at 250 °C. The time after beginning of nanocrystals growth (in seconds) is shown with *numbers on the lines*

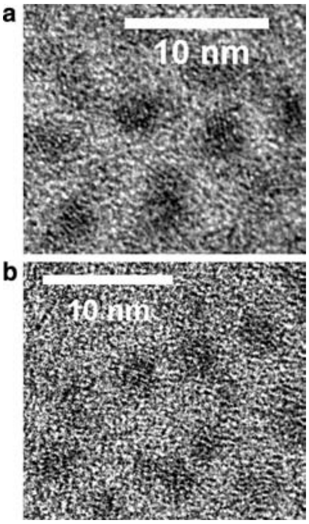

Fig. 3 High-resolution TEM images of (**a**) CdS (mean diameter 2.7 nm) and (**b**) CdSe (mean diameter 3.0 nm) nanocrystals prepared in paraffin matrix

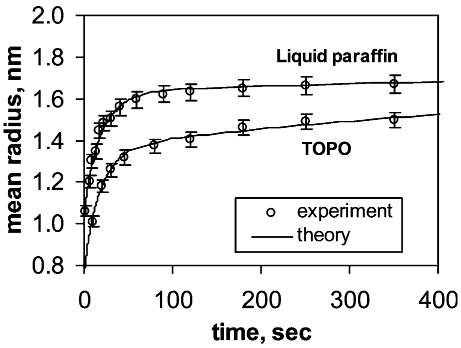

Fig. 4 Comparison between the temporal evolution of the mean CdSe nanocrystals radius in paraffin matrix and in TOPO matrix at 250 °C. The *solid lines* are theoretically predicted. The *error bars* are deviations from the mean value of two experiments

Table 1 Parameters of the numerical fits of data in Fig. 4

	R_0 (nm)	δ (nm)	R_r (nm)	R_d (nm)	τ_r (s)	τ_d (s)
Liquid paraffin	0.80	1.9	1.60	1.75	45	2,000
TOPO	0.75	1.9	1.44	1.55	55	1,000

R_0 is the radius of initial nuclei preceding the abundant nanoparticles; δ is the thickness of subsurface layer surrounding a nanoparticle; R_r and R_d are the limiting radii of fast and slow growth, respectively; τ_r and τ_d are the characteristic time constants of the fast and slow process, respectively

TOPO. In two of them cadmium acetate is used instead of CdO. First, $Cd(OAc)_2$ is heated together with stearic acid in paraffin to remove the crystal water and to form Cd-stearate. The addition of TBP-Se solution produces CdSe nanocrystals with almost similar growth rate compared to that when CdO is used for the in situ formation of Cd-stearate. Second, when we use $Cd(OAc)_2$ at the same conditions but without stearic acid, nanoparticles are obtained only in TOPO solvent, pure or with paraffin (their growth is very fast and significantly large nanocrystals are created). On the contrary, CdSe bulk material (large powder) is formed in pure liquid paraffin solvent (without stearic acid and without TOPO). The possibility to form nanocrystalline CdSe in pure TOPO by using $Cd(OAc)_2$ has been previously reported [8]. Use of $CdCl_2$ and $CdSO_4$ instead of $Cd(OAc)_2$ also results in the formation of bulk-sized CdSe in the tested conditions of paraffin with or without stearic acid. Obviously, these salts do not form Cd-carboxylate.

According to these results, the following suggestions can be made. In the Cd-carboxylate/TOPO system both TOPO and carboxylate ions have played a significant role to stabilize the nanocrystals (where carboxylate means stearate or acetate). This conclusion is proven by the formation of bulk CdSe in the absence of carboxylate ions (when $CdCl_2$ and $CdSO_4$ are used) or in the absence of TOPO (when paraffin is used). However, the presence of carboxylate ions is much more important than the free acid, since $CdCl_2$ and $CdSO_4$ could not form nanocrystals in the absence of carboxylate at all tested conditions. The chain of the carboxylate ion should be longer for better stabilization of the nanocrystals, e.g., stearate is more preferable than acetate. In the case of small carboxylate ion (acetate), TOPO plays a more significant role in the nanocrystal growth—the absence of TOPO in the $Cd(OAc)_2$/paraffin system leads to bulk CdSe.

Conclusions

A composite paraffin matrix, composed of thermoresistant organics and surface-active compound, can successfully replace TOPO in the formation of high quality A^{II} B^{VI} nanoparticles. The composite matrix has two functions: the container of nanospecies and the coordinating agent providing the formation and growth of nanoparticles. Each function comes from liquid paraffin (bulk medium) and stearic acid (surfactant), respectively. The stearic acid might form in the liquid paraffin a sort of aggregates like complexes or nano-micelles with the hydrocarbon tails facing the paraffin. However, such complexes or nano-micelles are thermally generated or destroyed and these processes should have fluctuative character. These nano-micelles, if existing, serve as the density fluctuations or nano-cavities in the matrix for the nucleation of the semiconductor nanocrystals. The longer the carboxylate chain, the better the stabilization of the nanocrystal in the nonpolar medium. Also, the longer carboxylate chain is a reason for the slower diffusion of the Cd-monomer in the solution and trough the subsurface layer around a nanoparticle. This slows down the reaction rate and provides better control over the nanocrystal growth. A combination of the paraffin solvent with TOPO may also provide fine control of the nanocrystals, depending on the TOPO concentration in the solution. For example, at higher TOPO to paraffin ratio the crystal growth rate will be slower and vice versa.

The paraffin composite matrix (liquid paraffin and stearic acid) is a low-cost and environmentally acceptable compound. This opens the way for manufacturing of semiconductor nanoparticles by the hot-matrix pyrolysis of precursors in the large scale.

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