Supplementary material (ESI) for Journal of Materials Chemistry

Ligand exchange of CdSe nanocrystals probed by optical spectroscopy in the visible and IR

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Supporting Information

Synthesis of CdSe particles and ligand exchange

Chemicals

Tri-n-octylphosphine oxide (TOPO, 99%, #22.330-1), tri-n-octylphosphine (TOP, 90%, 11.785-4), hexadecylamine (HDA, 90%, #H7.40-8), nonanoic acid (97%, #N5502), CdO (99.99+%, #20.289-4), Se (99.99%, #22.986-5), diethylzinc (#40.602-3), hexamethyldisilthiane ($(TMS)_2S$, #28.313-4), octanoic acid (>99.5%, #15.375-3), octanethiol (98.5+%, #47.183-6), and octylamine (99%, #O580-2) were purchased from Sigma-Aldrich. Tri-n-butylphosphine (TBP, 99%, #15-5800) was purchased from Strem. Dodecylphosphonic Acid (DDPA, technical grade) was purchased from Polycarbon Industries. A 20%wt stock solution of Se in TBP was prepared.

Synthesis of CdSe nanoparticles

The synthesis of CdSe nanoparticles was performed according to a previously described procedure by the Reiss group[1]. 5.76g HDA, 2.26g TOPO, 2.20g DDPA and 0.50g CdO were mixed in a 50mL flask. The powders were molten under nitrogen and then degassed for ca. 20 minutes at 130°C. Then the solution was heated under nitrogen atmosphere. At 290°C-300°C the color changed from brown to transparent. The solution should not reach a temperature higher than ca. 320°C, as at this temperature HDA would start to evaporate. Once the solution was clear, 1mL TBP was injected into the flask with a syringe and the remaining undissolved CdO was removed from the walls of the flask by agitating the flask. The temperature was then stabilized at 270°C and 1.6g of the Se:TBP solution was injected rapidly with a syringe into the solution. After ca. 1 minute the solution showed a light yellow color indicating the nucleation of CdSe particles. The reaction was allowed to proceed for 11 minutes, and then it was stopped by removing the heat-source. If the solution had been taken directly as it was after this step, the particles would have been embedded in a gel that had presumably been formed by polymerization of HDA, TOPO and DDPA. The following steps were done in order to prevent the trapping of the particles in the gel and to extract and purify them. The idea is to use nonanoid acid as surfactant to displace gel that has been bound to the particle surface.

When the solution had cooled down to below 100°C, 3mL of toluene, and 5mL of nonanoic acid were added to the flask. The particle solution was then precipitated immediately as soon as it had cooled down to below 40-50°C by addition of methanol. After removal of the supernatant by centrifugation the precipitate was dissolved in 5-10mL toluene. In some cases

[1] Reiss, P., S. Carayon, et al. (2003). "Low polydispersity core/shell nanocrystals of CdSe/ZnSe and CdSe/ZnSe/ZnS type: preparation and optical studies." Synth. Met. 139: 649-652.

the formation of a gel was observed. The particles were trapped in a big amount of organic material. Apart from the approach described above to remove the gel via addition of nonanoic acid, there are several slightly different approaches to extract the particles from the gel. Which of these approaches yields the best results depends on the nature of the sample and certainly also on the exact composition of the growth solution, i.e. on the type of impurity and thus ultimately on the producer of the individual compounds. Generally one should try to wash the sample as fast as possible after the reaction. On the other hand, the methanol for the precipitation should not be added at a too high temperature. All approaches used in our group involve the addition of a solvent as toluene or chloroform, nonanoic acid, and the precipitation of the particles with methanol. In the easiest case, it is sufficient to simply add a considerable amount (5-10mL) of nonanoic acid to the reaction solution when it has cooled down to ca. 100°C and then to precipitate the particles from the solution. Additionally the solution can be kept at ca. 90°C after the addition of the nonanoic acid and before the precipitation. This approach bears the danger of destroying the size distribution of the sample. In most cases we observed an enlargement of the fluorescence peak, and even the appearance of a second fluorescence line. A second approach is to first precipitate the particles out of the growth solution by addition of methanol. In this case, a sufficient amount (ca. 5mL) of toluene has to be added to the growth solution in order to prevent solidification of the organic material. Generally this yields a huge precipitate (particles in a gel) that is hard to dissolve in toluene. From this gel, the particles can be extracted by the addition of toluene and nonanoic acid in equal parts. By heavy agitation of the sample the gel can be dispersed in the solvent. Subsequent centrifugation yields a precipitate of the same size as the first precipitate and a very clear supernatant that is now colored red, indicating the presence of nanoparticles. The supernatant can be transferred carefully to another vial. By repetition of this process more particles can be extracted from the gel. In this process it makes a difference if one uses toluene or chloroform. Toluene is lighter than the gel, thus in the centrifugation the gel is found as the lower phase. When chloroform is used, the lower phase is the clear gel-free phase, and therefore it is fairly difficult to extract this phase from the vial without polluting it with the gel.

In all cases, once a gel-free solution has been obtained, the particles in this solution were washed to remove the residual free reactants. To do so, the particles were precipitated by addition of methanol to the solution and subsequently redissolved in toluene. Methanol for the precipitation was added until the solution turned completely cloudy. Generally this was the case when the ratio solvent to non-solvent was roughly 1:1. The purification step including precipitation and resolubilization was performed in total two times. After the purification the particles are well dispersed in toluene. At this step the particle surface is covered with a mixture of the following surfactants: TOPO, TOP, HDA, DDPA, nonanoic acid, whereby the respective ratios are unknown.

Ligand exchange

The synthesis of the nanocrystals as described above involves several surfactants. Their variety is prone to camouflage effects of ligand exchanges performed here. Thus, first a clean standard sample was prepared by exchange of the surfactants to only TOPO and TOP. To do so, we exposed the samples to a mixture of TOPO (99%) and TOP for 60 minutes at 130°C under inert conditions. 9g of TOPO were molten and degassed at 130°C. Then, under nitrogen 2mL TOP were added. Afterwards the nanocrystals dissolved in toluene were injected into this solution. After 60 minutes the solution was cooled down to room-temperature, and ca. 5mL toluene was added. The particles were washed by performing two precipitations with

methanol and subsequent re-dissolution in chloroform. At this point we expect the surface of the nanocrystals to be mainly covered by TOPO and TOP. These particles were used as reference system for our study.

Starting from these reference particles we performed controlled modifications on the surface of the nanocrystals. The sample was split into four fractions and on three of these fractions ligand exchange was performed. In all cases 5mL of the new ligand were heated to above 100°C and degassed. Then, under nitrogen, the CdSe-nanocrystals dissolved in toluene were added, and the solution was kept at ca. 110°C for 80 minutes. The ligands used were octanoic acid, octanthiol and octylamine. After the ligand exchange the particles were purified from residual free ligands by precipitating the particles twice with methanol. The particles were re-dissolved in chloroform. This yielded in total 4 samples of CdSe nanocrystals dissolved in toluene, with predominantly TOPO / TOP, octanic acid, actanthiol, and octylamine on their surface.

Discussion of the exchange rate

The major difficulty in determining the exchange rate resides in the fact that all surfactants used in this study exhibit strong absorption in the range between 1000 and 1700 cm^{-1}. Due to this overlap one can only make very qualitative statements on the contributions of the individual surfactants. In particular the amount of the individual surfactants cannot be inferred directly. At a first glance the line at 1720 cm^{-1} seems to be a good indicator for the presence of TOPO, at least when it is exchanged with a thiol or an amine. In these two cases this line almost disappears. On the other hand, the peak at 1090 cm^{-1} does not follow the same trend.

Here we try to estimate exchange rate under the assumption that we can actually extract data from the spectral range in question.

In the case of the exchange with octylamine, we might assume that the TOPO is washed away completely. The lines at 1720 cm^{-1} and at 1090 cm^{-1} disappear after the ligand exchange. Therefore we can assume that the contribution at 2960 cm^{-1} is only related to one surfactant. The contribution of the TOPO to this peak before the exchange is then:

$$A_{start} \propto 3 \cdot c_{TOPO}$$

The contribution of the amine after the exchange reads as:

$$A_{start} \propto c_{amine}$$

And therefore the number of the ligands increases after the exchange by the factor:

$$\frac{c_{amine}}{c_{TOPO}} = \mathbf{3} \cdot \frac{A_{exchange}}{A_{start}}$$

This value can be calculated to 1.6. Thus the number of surfactants is increased by 60%.
If we assume that the small peak found near 1720 cm^{-1} is related to TOPO, we can set up a slightly more complex model and assume that after the ligand exchange we find a higher density of surfactants and a mixture of TOPO and amine. In this case we can write for the ratio of the amplitude of the peaks at 2960 cm^{-1}:

$$\frac{A_{exchange}}{A_{start}} = \frac{c_{amine} + \mathbf{3} \cdot c_{TOPO}^{ex.}}{\mathbf{3} \cdot c_{TOPO}}$$

From the change of the area of the peak at 1720 cm^{-1} we can estimate that the amount of TOPO is reduced by a factor of 5 and we can calculate the ratio between the amines after the

exchange and the TOPO before the exchange to 1. In total, here we obtain an increase of the density of surfactants by 20%.
The same calculations can be made for the case of the exchange with thiol. If we assume that all TOPO was washed away and the line at 2960 cm-1 is only related to the thiol molecules, we find an increase of the density of surfactants by almost 100%. If now we assume that the peak at 1090 cm^{-1} can be ascribed only to the TOPO, we find that the amount of TOPO is reduced to 50% after the ligand exchange. With this value, we actually find that the total exchange ratio is very close to the value 1:1.

For the exchange with the octanoic acid it is actually hard to indentify any marker for the TOPO. Only from disappearing of the three features between 900 and 1200 cm^{-1} we could guess that the amount of TOPO is reduced to a minimum. With the assumption of the complete removal of the TOPO we find an increase of the density of surfactants by 50%.

Experimental errors

There are two major sources of uncertainty in our measurements. First the read-out of the spectra is subset to an error, which we estimated as 5%. The second source of error is the precise determination of the concentration of the nanocrystals in the samples. As all samples were of the same size, this error can again be reduced to the precision of the read-out of the absorption feature of the first exciton peak.(REFERENCE 27: Yu, Qu et al, 2003) Again, here we assume an error of 5% which is directly transferred into the amplitude of the absorption features in the IR-range.