1. Introduction

Nanometer-sized branched heterostructures are nowadays widely investigated because their optical and electronic properties can be tailored by a fine control of particle composition, size and morphology. Different phenomena such as quantum confinement of charge carriers, surface effects and confinement of phonons leading to these properties have turned these branched nanostructures into interesting materials with a variety of applications in optics.
Recently, Deka et al. developed a new method for the preparation of octapod-shaped colloidal nanocrystals via a one-pot cation exchange and seeded growth. Because of their symmetry, they also have excellent ability to measure small anisotropic forces. As a result of these properties and possible applications, several research groups have turned their attention to the synthesis and characterization of these nanostructures. The CdSe (core)/CdS (pods) octapods are synthesized through a cation exchange reaction of Cu$_{2-x}$Se in the presence of excess Cd$^{2+}$ ions, whereby eight wurtzite CdS arms grow on the [111] facets of a zinc blende CdSe core. The epitaxial growth relationship between the hexagonal arms and the cubic facets is: CdSe$_{1-x}$c(111)//CdS$_{1+x}$h(0001) and CdSe$_{1-x}$c[2-1-1]/CdS$_{1+x}$h[10-10].

It is well known that nanoscale materials display different thermal behavior from bulk materials. Their poor thermal stability (low melting point, shape changes, and tendency for coagulation) is a bottle-neck for a reliable integration in functional devices. In addition, the fabrication process itself often involves heating steps, e.g., when semiconductor nanoparticles are embedded in conducting polymer films to serve as solar cell material. In the case of heterogeneous nanostructures, the thermal stability is a much more complex property as not only there are multiple materials in nanoscale domains of different shape and size, but the domains may also interact with each other at elevated temperature, and even at room temperature. A good example thereof is the ripening of Au dots at the sides and tips of CdSe nanorods, whereby transport of Au atoms takes place from one Au dot to another, through the semiconductor nanorod material. The CdSe(core)/CdS(pods) octopods are a very nice example system to investigate the thermal stability of semiconductor-semiconductor nanostructures. Obviously, changes in the external morphology and the atomic arrangement of these nanostructures will influence their physical (structural, optical, and optoelectronic) properties.

Here, the thermal stability of both ex situ and in situ annealed CdSe/CdS octapods is investigated using a combination of various advanced transmission electron microscopy (TEM) techniques such as high resolution TEM (HRTEM), high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), electron tomography, energy filtered TEM (EFTEM) and in situ TEM with a heating holder. We show that both the morphology and the crystal structure change as a function of temperature. At low annealing temperatures (300 °C) we demonstrate that pure Cd segregates in droplets at the outside of the octapods, indicating non-stoichiometry. Furthermore, we found that the pods lose their faceting and become rounded. Heating to higher temperatures induces the zinc blende core to grow and sublimation of the octapods first occurs at the four pods pointing into the vacuum.

2. Results

2.1. As-synthesized Octapods

As-synthesized, non-heated CdSe/CdS octopods were investigated by TEM. Conventional TEM images are presented in Figure 1a and Figure 1b. These images show that the octapods have four flat ended pods and four pencil-shape ended pods. This is also in agreement with a 3D visualization of these octapods obtained by electron tomography. The tomographic 3D reconstruction created from different HAADF-STEM projections is shown in Figure 1c–e. Both the tomographic reconstruction and the HAADF-STEM projection shown in Figure 1f indicate that all the pods have three dominant side facets and three smaller facets. A full movie of the tomographic reconstruction is available in the supporting information (M1). High resolution HAADF-STEM studies (Figure 1g and 1h) confirm that the core has a cubic zinc blende crystal structure whereas the pods have a hexagonal
wurtzite structure with their long axis along the [0001] direction, extending along the [111] directions of the cubic zinc blende core. Figure 1g shows a high resolution HAADF-STEM image from a hexagonal wurtzite pod viewed along the [0001] direction of the pod. From this figure, it can also be seen that the pods have 3 dominant {11-20} facets and 3 smaller {10-10} facets. Figure 1h shows the cubic zinc blende lattice of the core of the octapod after tilting to the [001] direction. STEM-EDX mapping of the octapod indicates that the pods have non-stoichiometric composition where the ratio between Cd and S equals 1.151 ± 0.061.

2.2. Heating to 300 °C: Shape Change and Cd Segregation

In order to investigate the thermal stability of the octapods at elevated temperatures, in situ annealing experiments are performed in which the octapods are heated to a temperature of 300 °C. At this temperature, conventional TEM images (Figures 2a and 2b) show that all the pods have acquired a more rounded shape instead of the original flat ended and pencil-shape ended pods. To confirm the change of the morphology in 3D, electron tomography is performed on ex situ annealed octapods at a temperature of 300 °C. One of the HAADF-STEM projections used to make the 3D reconstruction is displayed in Figure 2c and a visualization of the reconstruction is presented in Figure 2d. From this figure, it is again clear that all the pods show a more rounded shape. A full movie of the reconstruction is available in supporting movie M2. The slice through the reconstruction displayed in Figure 2e furthermore indicates that pure Cd has segregated as droplets that are attached to the ends and the sides of the CdS pods. These droplets appear with a higher intensity in the image in comparison to the rest of the octapod because the intensity in a HAADF-STEM projection scales with Z^{1.7} (with Z the atomic number of the chemical element). This observation is also confirmed by EFTEM imaging of the octapod (Figures 2f–2h) indicating that the droplets contain pure Cd and no S.

2.3. Heating to 500–700 °C: Sublimation

Slow in situ annealing to a temperature of 600 °C induces rounding of the pods followed by sublimation. This process is displayed in Figure 3 which reports frames from a recorded movie with frame times of 0.25 s (the full movie is available in supporting movie M3). The total time span of the sublimation shown in the figure is 500 s. When the original octapods are swiftly heated to a higher temperature of 700 °C, no rounding of the pods is observed before sublimation. Frames from a recorded movie of these sublimating octapods are reported in Figure 4 (the full movie is available in supporting information M4). The recording time of a frame is 0.25 s and the total time of the sublimation equals to 260 s. In this case, the pods are not given the time to reshape to rounded ends prior to sublimation. No deformation of the SiN grid was observed at these high temperatures. In the case of the swift heating to 700 °C (Figure 4, Movie M4), the CdSe cores appear to sublimate sooner than the CdS pods. Here we remark that the melting temperature of bulk CdSe is lower than that of bulk CdS (1239 versus 1750 °C, respectively), and that although the “nanoscale” sublimation temperatures observed in this work (500–700 °C) are considerably lower,
CdSe may sublimate sooner than CdS when having similarly small dimensions. A close inspection of Movie M3 reveals that four of the pods sublimate first, followed by a second set of four pods. Because the pods are overlapping pairwise in this projection, it is not clear which pods (pointing to the support or into the vacuum) sublimate first. To further investigate this, electron tomography was used to visualize partly sublimated octapods. Because the MEMS microheaters that were used for the in situ annealing studies do not allow the high-tilt imaging required for electron tomography, octapods were drop-cast onto a C grid (Quantifoil) and heated ex situ in a vacuum furnace at an elevated temperature of 500 °C (annealing to higher temperatures is not possible because of degradation of the C grid). One of the 2D HAADF-STEM projections is shown Figure 5a. The visualization of the tomographic reconstruction displayed in Figure 5b indicates that some of the pods are sublimated while others remain intact and have a rounded shape. The reconstruction shows that the arms that have sublimated most are those that are not in contact with the C grid. The supporting C grid is indicated in the visualizations of the reconstruction, but this is not visible in the final reconstruction because of the high contrast between Cd and C in the HAADF-STEM projections. From the slice through the reconstruction displayed in Figure 5c, it can be seen that no segregation of Cd is observed at the pods. A full movie from the tomographic reconstruction is available in the supporting information (M5). HRTEM studies of these ex situ heated octapods at 500 °C show that the zinc blende core grows at the expense of the pods, which indicates that part of the wurtzite material transforms into the zinc blende structure of the core. A HRTEM projection of the zinc blende core is shown in Figure 5f. However, it is also noticed by these HRTEM studies that the shrunken pods do not transform completely into zinc blende, but retain their wurtzite crystal structure. This can be seen in Figure 5g where the lattice spacing of 3.2 Å corresponds to the distance between the [10-11] planes of the hexagonal wurtzite structure.
3. Discussion

At all elevated temperatures (300–700 °C), the morphology of the octapods changes and both the flat-ended and the pencil-shaped pods become rounded. This rounding is likely caused by temperature related thermodynamic entropy effects that render the energy differences between the different facets negligible. Comparable features are found for PbSe nanoparticles in a range of a few hundred degrees below the melting point, which is usually referred to as “surface roughening”.[33] Another possibility is that the heat treatment in vacuum may lead to a decomposition of the ligands bound to the polar facets and loss of their chemical activity, resulting in a loss of faceting.

This rounding of the pods will influence both the optical and electronic properties of the octapods and has to be taken into account in the possible applications of these nanostructures. Optical properties of nanoparticles are to a large extent determined by their 3D morphology. For example, Perassi et al. found that both the far and near-field optical properties of Au nanoparticles change drastically with only small differences in the morphology such as deviations from perfect crystal facets.[32] It can therefore be expected that the rounding of the pods observed here will have major influence on the functionality of the nanostructures.

At temperatures just below the sublimation temperature of the octapods, segregation of pure Cd is observed at the side and the tips of the pods of the octapods. This is likely due to an initial deficiency in S (or an excess of Cd) in the as-synthesized octapods. This is also confirmed by STEM-EDX mapping of the pods. Off-stoichiometric compositions are not uncommon for colloidal semiconductor nanocrystals as has been shown previously for PbSe nanocrystals.[33,34] Furthermore, we remark that samples (solutions) are never completely cleaned from precursors, and therefore residual Cd-phosphonate complex may be present on the grid. As a result of heating, neutral Cd atoms may be formed from these precursors, which migrate along the grid and start adding up to the tips of the octapods. The latter effect is probably a minor contribution, as no agglomeration of Cd was observed in ‘empty’ areas of the support. At higher temperatures, sublimation of the pods is observed where the pods that are not in contact with the C grid are the first to sublime. This implies, first of all, that the contact with the C grid has a stabilizing effect on the octapods.

The thermal stability of CdSe/CdS octapods has been investigated using both ex situ and in situ heating experiments. Whereas the original octapods have four pencil-like ended pods and four flat ended pods, rounding of the pods is observed at all elevated temperatures. At low annealing temperatures, pure Cd segregates in droplets at the side and the tip of the pods. Further heating to temperatures just below the sublimation temperature of the octapods induces the zinc blende core of the octapod to grow at the expense of the wurtzite pods. At higher temperatures (500–700 °C), sublimation of the octapods is observed where the pods that are not in contact with the C grid are the first to sublime.

4. Conclusion

The thermal stability of CdSe/CdS octapods has been investigated using both ex situ and in situ heating experiments. Whereas the original octapods have four pencil-like ended pods and four flat ended pods, rounding of the pods is observed at all elevated temperatures. At low annealing temperatures, pure Cd segregates in droplets at the side and the tip of the pods. Further heating to temperatures just below the sublimation temperature of the octapods induces the zinc blende core of the octapod to grow at the expense of the wurtzite pods. At higher temperatures (500–700 °C), sublimation of the octapods is observed where the pods that are not in contact with the C grid are the first to sublime.

5. Experimental Section

In situ heating of the octapods is performed using a MEMS microheater in a cubed TITAN microscope with aberration correction, operating at 300 kV.[35] The MEMS microheater contains an embedded, 200-nm-thick coiled Pt heating wire. The solution with octapods is drop-casted onto the chip, and the octapods can then be imaged on electron-transparent, 15-nm-thick viewing windows that are present between the windings of the wire. Ex situ heating is performed in a vacuum furnace just before inserting the samples into the electron microscope. The annealing times are 15 min for the octapods heated to 300 °C and 30 min for the octapods heated to 500 °C. Electron tomography experiments are all acquired using a TecnaiG2 microscope operating in HAADF-STEM mode with a camera length of 70 mm and using a dedicated Fischione tomography tilted holder. For every tilt series, projections are recorded over a tilt range of ±70° with an increment of 2°. Alignment and reconstruction of the tilt series are both done using the FEI Inspect3D software. For all the tilt series, a SIRT algorithm is used with 25 iterations. High resolution TEM imaging is performed.
on a cubed TITAN 50-80 microscope operating at 300 kV. HRSTEM images are acquired in the same cubed TITAN microscope using a camera length of 183 mm and the EFTEM elemental maps are recorded with a Philips CM30 microscope, using the jump ratio method. Therefore, two images for the Cd M_{4,5} edge (58 and 77 eV) and two images for the S L_{2,3} edge (153 and 177 eV) are recorded with a slit width of 10 and 20 eV, respectively. The recording times are 4 s for the acquisition of both elements. Quantification of STEM-EDX measurements is performed by averaging over 10 different spectra all acquired with a TecnaiG2 microscope using an integration time of 30 s.

Supporting Information

Supporting Information for this article is available online and includes two sublimation movies (M3, M4) of in situ heated octapods. Also three movies with a visualization of the tomographic reconstructions of non-annealed octapods, octapods annealed at 300 °C and octapods annealed at 500 °C are available on-line (M1, M2, and M5).

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