Morphological and chemical transformations of single silica-coated CdSe/CdS nanorods upon fs-laser excitation†

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Radiation-induced modifications of nanostructures are of fundamental interest and constitute a viable out-of-equilibrium approach to the development of novel nanomaterials. Herein, we investigated the structural transformation of silica-coated CdSe/CdS nanorods (NRs) under femtosecond (fs) illumination. By comparing the same nanorods before and after illumination with different fluences we found that the silica-shell did not only enhance the stability of the NRs but that the confinement of the NRs also led to novel morphological and chemical transformations. Whereas uncoated CdSe/CdS nanorods were found to sublime under such excitations the silica-coated nanorods broke into fragments which deformed towards a more spherical shape. Furthermore, CdS decomposed which led to the formation of metallic Cd, confirmed by high-resolution electron microscopy and energy dispersive X-ray spectrometry (EDX), whereby an epitaxial interface with the remaining CdS lattice was formed. Under electron beam exposure similar transformations were found to take place which we followed in situ.

Introduction

Heterostructured semiconductor nanoparticles (NPs) have attracted much scientific attention due to their tunable optical and electronic properties.1,2 They display unique size and material dependent emission and absorption properties that are of great interest for various applications such as light-emitting diodes (LEDs),3 lasers,4–6 sensors7 and biological imaging.8 Among the vast array of morphologies of heterostructured semiconductor NPs, CdSe/CdS nanorods (NRs) are intriguing systems as they exhibit quantum yields up to 75% and reduced blinking.9–11 Such NRs consist of a spherical CdSe core and an elongated CdS shell in which the core is asymmetrically positioned towards one end of the rod. The charge separation of the carriers can be influenced by depositing a metallic centre which is used for electro-optical modulators,12 optical switches,13 nano-thermometers,14 photocatalysis15,16 and photovoltaics.17 The emission and absorption are polarized which can be exploited in polarized LED’s18 but could also be used in improved data storage as has been demonstrated for gold nanorods.19 Furthermore, the extinction coefficients for multiple photon absorption in CdSe/CdS NRs are significantly higher than for CdSe quantum dots making them interesting for non-linear optical applications as well.20,21

For many applications, the chemical and (photo)thermal stability of CdSe/CdS NRs is still a serious issue. Several solutions were proposed to overcome the stability problems. In particular, complex multishell heterostructures, such as CdSe/CdS/ZnS, proved promising but require a more complicated synthetic procedure.8,22,23 Alternatively, a silica coating is known to enhance the thermal and colloidal stability of NPs and dyes.24–27 This has also recently been shown for CdSe/CdS NRs where a silica coating resulted in increased photostability under UV irradiation and chemical stability under O2 exposure with respect to the same uncoated NRs.28 It has not been explored so far, however, how chemically and morphologically stable silica-coated CdSe/CdS NRs are upon irradiation, when e.g. exposed to an electron beam or to fs-laser pulses which are used in several applications and/or particle characterization methodologies. This is important to study since different morphological modifications of the particles under study can result in completely new structures. It was shown, for example, that Au-tipped CdS NRs underwent chemical transformations...
upon high-density electron beam irradiation exhibiting new phases that would not be stable in bulk.\textsuperscript{29} Such transformations were not observed for NRs without a Au-tip or when the NRs were simply heated without radiation-induced effects.\textsuperscript{29,30} Such radiation-induced modifications are interesting from a fundamental point of view but also for stability reasons. Understanding the interaction of these systems in silica shells also helps to design and optimize silica-coated hybrid metal–semiconductor structures.\textsuperscript{31} Additionally, contrary to sphere-like quantum dots, NRs often have a non-equilibrium shape which plays an important role regarding stability as is seen for gold NRs for which the metastable shape is unstable at temperatures far below the melting temperature.\textsuperscript{32} Studying such changes and transformations can reveal novel nanostructures and interesting nanoscale phenomena.

We performed fs-two-photon excitation experiments on silica-coated CdSe/CdS NRs and monitored the structural changes of individual particles after fs-pulse excitation. The experiments were conducted at different laser intensities while analyzing the same particles before and after fs-laser excitation with transmission electron microscopy (TEM). We observed that with increasing laser power the particles first broke into two or more anisotropic fragments which then independently deformed into a more spherical shape. Additionally, Cd-rich domains were formed out of the remaining (mainly) CdS phase which was revealed by high-resolution scanning transmission electron microscopy (STEM) and EDX. While very similar results were obtained under electron beam excitation, heating did not result in such transformations. These findings are different in comparison to the same NRs without a silica-coating or with only a partial coating, where we found sublimation of CdS without deformation, showing that physical confinement can dictate morphological and chemical changes.

### Experimental methods

The CdS NRs with a spherical CdSe core were synthesized following a seeded growth approach.\textsuperscript{9} The rods were 46 nm ± 4 nm long and 4.6 nm ± 0.6 nm thick and had a CdSe core size of 3.2 nm. A silica shell of about 10 nm was grown around the CdSe/CdS NRs following Hutter \textit{et al.}\textsuperscript{33} The absorption and emission as well as TEM images of these NRs before and after silica growth are presented in Fig. 1. The first absorption peak of the CdS shell was at 460 nm. Due to the larger volume of the shell compared to the core, absorption is governed by the CdS shell\textsuperscript{33} whereas emission stems from the CdSe core and is red-shifted as CdSe has a smaller band gap than CdS. For the femtosecond laser excitation a Leica SP8 confocal setup with an integrated Ti:Sapphire laser (Coherent chameleon II, 80 MHz repetition rate, 140 fs pulses) was used where the particles could be found back on the TEM grids. The Ti:Sapphire laser can be tuned from 670 nm to 1080 nm. We chose 920 nm as excitation wavelength since it mimicks a two-photon excitation of the NRs. A thin 3D stack was scanned with a pixel size of 22.6 nm × 22.6 nm pixel size, a pixel dwell time of 1.2 μs and a total scan time of about 20 s. Details can be found in the ESI.\textsuperscript{†}

### Results and discussion

In order to study the structural changes of the CdSe/CdS NRs after fs-laser excitation, different laser fluences were applied and morphological changes were observed by TEM. The upper row in Fig. 2a shows the particles before laser excitation and the second row displays the same particles after fs-laser excitation of different fluences. For the lowest applied peak fluence of 2.6 mJ cm\textsuperscript{−2} the particles did not change their shape as displayed in the first column of Fig. 2a. At the highest fluence of 8.7 mJ cm\textsuperscript{−2} most semiconductor NRs sublimated leaving empty silica shells behind as can be seen in the last column in Fig. 2a. Interestingly, after fs-excitation with an in-between laser fluence of 5.8 mJ cm\textsuperscript{−2} differently shaped semiconductor particles were found in a mostly intact silica shell as shown in the two middle columns in Fig. 2a. In some cases (arrows in left column) the NRs broke into 2 rods with about half of the length of the original rod keeping a thickness of about 5 nm. In other cases two shorter fragments of increased thickness (about 6.5 nm) were found inside the silica shells, as highlighted by the upper arrow in the right column. These fragments deformed as their shape was more spheroidal than rod-like. Spherical fragments with diameters of about 8 nm were also found as shown in the right column of the middle box in Fig. 2a (lower arrow). The NRs mainly fragmented into two pieces although one or three and sometimes more than 3 fragments were also observed (Fig. S2†). The deformed particles most likely decreased in volume as estimated from comparing the volume of the same rod before and after fs-laser excitation indicating that the CdS partially decomposed and/or sublimated to some extent as well at the intermediate fluence and not only at the highest one shown in Fig. 2a. However, this needs to be considered with care since TEM images are just 2D projections.

The silica shells have a stabilizing effect, almost certainly of kinetic origin, at least against the sublimation of CdS, since the
same uncoated NRs disappeared even under the lowest fluence of 2.6 mJ cm\(^{-2}\) (Fig. S4a†). The same was true for particles where the silica did not fully cover the NR which allowed for easier sublimation (Fig. S4b†). The latter indicates that the observed breaking and deformation only happened because of the confinement of the silica shell since it delayed the evaporation of CdS forcing the system to react to the absorbed energy in a different way. Breaking up of the semiconductor NRs was not observed for uncoated NRs and in situ heating experiments of uncoated CdSe NRs.\(^{30}\) The deformation of uncoated CdSe/CdS NRs to a spherical shape under fs-pulse excitation was observed previously.\(^{35}\) However, from these experiments it was not clear whether these were remnants of sublimated NRs and/or really deformed fragments of the original NRs.

In order to obtain a better understanding of the morphological transformations observed in Fig. 2a, STEM and EDX measurements were performed as well. STEM images of the different particle shapes are presented in Fig. 2b. The left and middle images in 2b show a close-up of some particles from the middle columns in Fig. 2a. In most cases (but certainly not all), and especially for the semiconductor particles within the shells that were more deformed after fs-excitation, a bright spot was observed at the tips of the fragments. The spot increased relatively in size with respect to the remaining particle/fragment for higher deformation degrees as shown in Fig. 2b. Inherent to imaging in high-angle annular dark-field (HAADF) STEM mode is the \(z\)-contrast whereby heavier elements appear brighter. Thus, the bright spots cannot be CdS or CdSe as these would have a similar STEM contrast. Pure Cd would give a higher STEM contrast. To verify the presence of metallic Cd a high-resolution STEM image was taken of such a fragment. The image together with diffractograms of both parts of the fragment are shown in Fig. 2c. For the less bright part of the fragment (right diffractogram) we obtained lattice spacings of 0.310 nm and 0.299 nm. These are in reasonable agreement with the calculated values of 0.318 nm for the (101)\(\bar{1}\) and (011)\(\bar{1}\) lattice spacings in wurtzite CdS (details in ESI†). Notably, the lattice was slightly tilted since the two measured values are not the same. For the bright part of the fragment (left diffractogram) we obtained spacings of

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**Fig. 2** Deformation stages at different laser fluences. (a) TEM images of the same silica-coated CdSe/CdS NRs before (top row) and after (bottom row) excitation with fs-laser pulses of three different peak fluences. The arrows mark examples of three different shapes found after illumination. (b) HAADF-STEM images of the three different shapes obtained after excitation with 5.8 mJ cm\(^{-2}\) pulses. (c) HR-STEM image of a typical fragment. The insets show two diffractograms corresponding to the two different parts of the fragment (see text for details).
0.225 nm and 0.218 nm which corresponds to the calculated spacings of 0.235 nm for the (101) and (011) planes for hexagonal close-packed Cd. Similar to the CdS lattice the crystal was slightly tilted. Thus, the high-resolution STEM image confirms that metallic Cd segregated at the tips of the NRs. Interestingly, both lattices were found in the same crystallographic orientation. This shows that laser annealing can lead to an epitaxial, strong and extended metal–semiconductor interface, an important topic in nanoscience. Possibly a similar ‘fs-laser-writing’ methodology can be applied to create epitaxial interfaces with other hcp metals such as Mg, Ti, Co or Zn. This cannot be simply achieved by heating the NPs as we did not observe such transformation during in situ heating experiments indicating that the type of energy deposition matters (Fig. 4). The location of the segregated Cd spots was observed to be often located at one end of the original CdSe/CdS NR and the formed fragments. We did not observe a preference of Cd segregated spots of neighboring fragments to point toward or away from each other.

In order to further confirm whether the segregated parts were Cd we performed STEM–EDX chemical mapping measurements on these particles. Fig. 3a and b show the count rate maps for the particles also shown in the middle and right images in Fig. 2b, respectively. The EDX measurements confirmed that the brighter spots observed with STEM were indeed Cd, whereas the rest of the particle was CdS. The Se which is in principal present in the core of the particles could not be mapped (Fig. S7†). That does not necessarily mean that no Se was present anymore. Due to the beam sensitivity of the material the EDX maps could only be taken for a relatively short time (306 s and 210 s for the maps in Fig. 3a and b, respectively). Since the core is only 3 nm small this might not be enough time to acquire sufficient counts to detect the Se. It is good to mention that under similar EDX acquisition conditions the CdSe core could also not be detected for undeformed silica-coated NRs (Fig. S8†). For that reason the core position is normally determined by elaborate analysis of high-resolution TEM or STEM images. It is known, however, that the core of core/shell semiconductor nanoparticles can oxidize and consequently shrink upon heating or irradiation. Thus, although the impact of laser heating is different to oven or in situ heating, it would not be surprising if the core was not present anymore after the applied 5.8 mJ cm⁻² laser pulses. The three marked fragments in Fig. 3a and all fragments in Fig. 3b were quantified with the Cliff-Lorimer method. Whereas the fragments in Fig. 3a

![Fig. 3 Results of STEM–EDX chemical mapping performed on the fragments obtained after fs-excitation. (a) HAADF-STEM image and count rate maps of Cd, S, Si and the overlay of Cd and S for spheroidal fragments obtained after excitation with 5.8 mJ cm⁻² as shown in the middle image in Fig. 2b. By quantification of the three circled fragments we obtained a Cd : S ratio of about 50 : 50. (b) HAADF-STEM image and count rate maps of Cd, S, Si and the overlay of Cd and S for spherical fragments obtained after excitation with 5.8 mJ cm⁻² as shown in the right image in Fig. 2b. Quantification of the fragments revealed a Cd : S ratio of 56 : 44. All scale bars represent 20 nm.](image-url)
exhibited a Cd : S ratio of 50 : 50, which is similar to the Cd : S ratio of the undeformed silica-coated NRs (see Fig. S8† for details), the fragments in Fig. 3b contained an excess of Cd with a Cd : S ratio of 56 : 44, which is expected due to an increased amount of segregated Cd.

On a side note but worth mentioning, under kHz excitation conditions uncoated CdSe/CdS NRs of similar size were shown to withstand higher fluences as shown for two-photon pumped amplified spontaneous emission experiments.\textsuperscript{2,6} Furthermore, for data storage experiments under MHz excitation, \textit{i.e.} where the inhibition of luminescence is desired, the amount of absorbed pulses played a role as well.\textsuperscript{35} Thus, heat accumulation is an important factor for the photostability of CdSe/CdS NRs for high repetition rate lasers.

However, the chemical and morphological transformations observed here are not purely heat-induced as \textit{in situ} heating experiments only lead to sublimation of the material without CdS decomposition. Fig. 4 presents results of heating experiments performed \textit{in situ} in an electron microscope. Fig. 4a shows STEM images of the same spot followed over different temperatures. The indicated time is the heating time at that temperature when the STEM image was taken. The zoom was kept at relatively low magnification to avoid electron-beam induced deformation of the NRs as shown in Fig. 5. The particles were unchanged up to 400 °C. At 450 °C particles started to sublime and sublimation increased with temperature. At 700 °C about half of the particles sublimated whereas the rest remained almost completely intact. The particles that sublimated were mainly NRs that were not fully covered by the silica shell, similarly to the fs-laser excitation (Fig. S4†). It is remarkable that most particles that were fully covered by the silica shell stayed stable up to such high temperatures although it is known that the thermal stability drastically decreases for nanomaterials.\textsuperscript{41,42} However, it is known that the electron beam can cause the deposition of a thin carbon shell around the particles which stabilizes them tremendously. Such

![Fig. 4](https://example.com/fig4.jpg)
a behavior was seen for in situ heating experiments on gold and silver nanorods. Despite the reduction of the electron beam exposure by parking the beam at the lower left corner or blanking it in between images, the influence of such a carbon shell cannot be neglected. Fig. 4b shows zoomed-in STEM images of the spot in (a). These images were taken subsequently after either changing the temperature or after an increased amount of time as indicated. Partial and complete evaporation of single NRs is highlighted by arrows. It can be observed that the NRs did not deform to spheroidal or spherical shapes prior to sublimation. The left over fragments kept their width after partial sublimation. It should be noted that some NRs exhibited small Cd segregated spots (one is marked by the white square) which is ascribed to the electron beam irradiation as they were not found for NRs that were heated without prior electron beam exposure (Fig. 4c).

In order to check the influence of the electron beam and circumvent the carbon shell creation, different windows on the heating chip were visited at 300 °C, 450 °C, 500 °C, 600 °C and 700 °C. These windows had not been exposed to the electron beam before. Examples of different heating windows at different heating times are shown in Fig. 4c. The sublimation also started around 450 °C but was more severe than observed in Fig. 4a. This indicates that indeed a carbon shell was protecting the particles in Fig. 4a. Interestingly, the NRs also broke into fragments as observed for fs-illumination. As mentioned in the main text, this is a result of the silica confinement as it was not observed for uncoated CdSe NRs. Similarly to our work, these authors observed sublimation of CdSe NRs without deformation or chemical transformation of the NRs to spherical shapes. In agreement with that, work performed by Reichert et al. showed that CdSe and CdS NRs were compositionally stable up to 700 °C in an inert atmosphere. Our findings and the observations of Hellebusch et al. and Reichert et al. strengthen our hypothesis that the deformation and chemical transformations upon laser irradiation are not a purely heat-induced effect. Heat was shown to speed up the radiation-induced effects though.
A further proof that the observed transformations are radiati
ation-induced is that the NRs transformed similarly under
electron beam exposure. During the EDX and high-resolution
STEM image acquisition we observed that part of the deformed
fragments could also further deform under the electron beam.
Furthermore, the segregated Cd sometimes appeared, grew or
even dissolved again under the electron beam (Fig. S5†). A few
about 1 nm or smaller Cd spots could also sometimes be
observed at the surface of the undeformed NRs within the
silica shell (Fig. S3†). This might stem from an excess of Cd-
ions during the synthesis which were reduced by the electron
beam and aggregated or alternatively from a slight evaporation
of S or Se, but these dots are not enough to form the large
bright Cd spots as observed after fs-illumination. Such a Cd
segregation is energetically favoured over single Cd atoms
and was also observed during in situ heating of CdSe/CdS octapods
due to non-stoichiometric conditions. A similar process is
also known for Au on CdS NRs where isolated Au clusters were
found to combine into one domain at the tip of the CdS NR
upon heating.37

Due to the electron beam sensitivity of the nanorods we
decided to follow the radiation-induced damaging and transform-
ations of the CdSe/CdS NRs inside the silica shells in situ
in the TEM under the impact of the electron beam (probe
current of 506.4 μA). Fig. 5a shows a series of HAADF-STEM
images as a function of e-beam irradiation time. First, the
nanorod began to thin at one spot (35 s) where it then broke
(70 s). Then, a second part thinned (70 s, 105 s) at which point
the particle broke a second time (140 s, 175 s). The three frag-
ments deformed further to a more spherical shape (210 s,
280 s). Additionally, a bright spot occurred after around 140 s at
the highest fragment and grew further over time until it was
bigger than the rest of the fragment (Fig. S6†). EDX measure-
ments of the obtained fragments confirmed that the bright spot
was Cd (Fig. 5b). Thus CdS must have decomposed as the CdS
volume was decreasing whereas the Cd volume was increasing.
As mentioned before, decomposition of CdS and agglomera-
tion of Cd atoms as metallic Cd was observed earlier under
the influence of an electron beam for Au-tipped CdS NRs.19 EDX
quantification of the elongated fragment at the bottom and the
upper fragment with the segregated Cd revealed that while the
elongated fragment had a Cd : S ratio of 53 : 47 (similar to
undeformed NRs) the upper fragment showed a clear Cd excess
with a Cd : S ratio of 74 : 26. This indicates that CdS was not
only decompoud but that S must have sublimated or left the
system otherwise.

By comparing the experiments under fs-laser and electron
beam excitation it can be seen that the impact of both exci-
tations is quite similar as the obtained shapes and resulting
chemical compositions are alike. Since the particle in Fig. 5
first broke into rod-like fragments which afterwards deformed
into more spherical shapes, we believe that the shape in the
left image of Fig. 2b was formed at lower absorbed energies
than the other two. The particles in the right column absorbed
most energy from the laser fluence with respect to the other
two and deformed further. Although the in-between shapes
were observed for the same laser fluence it does not mean that
all the particles absorbed exactly the same amount of energy.
The fluences were calculated for the focal plane (see ESI†).
Due to the high numerical aperture of the confocal setup,
however, small inhomogeneities in height lead to differently
absorbed energies, as described in more detail in ref. 25.
Furthermore, the nanorods exhibit polarized absorption
meaning that particles aligned with the laser polarization
direction absorb more than the ones perpendicular to it.16 For
these reasons, particles lying in the illuminated area of about
12 μm × 12 μm experienced slightly different fluences leading
to the different shapes.

The observed deformation mechanism is illustrated schemati-
cally in Fig. 6. The nanorods first break into two or more rod
fragments. The individual fragments then deform via shorter
rods to an eventually spherical shape. The fragments decrease
in volume due to decomposition and sublimation of CdS.
The left-over Cd atoms after CdS decomposition form metallic Cd
which segregates at one end of the fragments. Left-over S most
likely sublimated. However, it needs to be mentioned that not
all fragments show metallic Cd spots. Finally, if more energy is
absorbed, the NRs completely sublimate through the silica shell
as seen the last column in Fig. 2a.

Conclusion
In conclusion, we studied the morphological and chemical
transformations of silica-coated CdSe/CdS NRs. We found that
the silica-coating enhanced the photostability under fs-pulses.
Furthermore, the NRs transformed under the impact of fs-
laser pulses or electron beam exposure by breaking into frag-
ments which deformed to more spherical shapes. In the
process, CdS partly decomposed which led to the segregation
of metallic Cd. The resulting Cd and CdS crystals were found
to have a well-defined orientation relationship and having an
epitaxial interface between the crystals. The confinement by
the silica shell played a critical role in this process as un-
covered CdSe/CdS NRs were found to just sublimate without
any transformations. Hence, there is still a lot to learn about
the often out-of-equilibrium interaction of radiation and nano-
structures. Novel nanostructures and epitaxial metal–semi-
conductor interfaces can be made by fs-laser excitation. These
experiments show that fs-laser excitation opens a new way of
nanoparticle tuning as it can transform the morphology and
chemical composition in a controlled way in a small volume.
They also raise questions, however, about the chemical and
morphological stability when using these NRs in devices that
are subject to application-related prolonged irradiation.
Author contributions

A. v. B. initiated and supervised the project. E. M. H. synthesized the particles under the supervision of D. V., W. A. performed the fs-laser experiments and TEM measurements on the same particles before and after excitation as well as the in situ heating experiments. B. G. performed the STEM and EDX measurements under the supervision of S. B., M. v. H. facilitated the in situ heating electron microscopy measurements and helped in explaining the experimental results. All authors discussed results and gave feedback on the written manuscript.

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