

# Segmented CdSe@CdS/ZnS Nanorods Synthesized via a Partial Ion Exchange Sequence

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**(5)** Supporting Information

**ABSTRACT:** In this communication we present a synthetic pathway toward CdSe@CdS/ZnS nanorods which are built in a segment like manner (a CdSe core which is embedded in a CdS rod which then epitaxially ends in a ZnS rod). This structure is realized exploiting a sequential cation exchange mechanism. In a first step, CdSe@CdS rods are transformed into CdSe@CdS/Cu<sub>2-x</sub>S rods. In a second step, the latter ones



are converted into CdSe@CdS/ZnS rods. By varying the amount of Cu<sup>+</sup> precursor in the Cd<sup>2+</sup> to Cu<sup>+</sup> ion exchange step, the phase boundary between CdS and ZnS can be shifted in a controlled manner. This finding nicely demonstrates that cation exchange reactions in nanocrystals can not only be used to exchange the complete cation lattice but also only specifically selected parts of it. The obtained CdSe@CdS/ZnS nanorods are optically and electron microscopically characterized in depth.

# ■ INTRODUCTION

Semiconductor nanoparticles are nowadays a well-known material class which is investigated fundamentally as well as for a large variety of applications (e.g., solar cells, LEDs, photocatalysis, etc.).<sup>1</sup> The colloid chemical approach and here especially the so-called "hot injection" approach, in which precursors are combined in a mixture of high boiling coordinating solvents, is particularly attractive due to the low degree of polydispersity of the obtained samples as well as due to the high degree of shape and composition control achievable. Consequently, today many more semiconductor particles than simple single component spherical particles (so-called quantum dots) can be synthesized. Among the structures realized so far are spherical core@shell particles,<sup>2,3</sup> elongated quantum rod structures,<sup>4</sup> tetrapods,<sup>5</sup> core@shell rods,<sup>6</sup> seeded rods,<sup>7–9</sup> and seeded multipods (e.g., seeded tetrapods<sup>10</sup> and seeded octapods).<sup>11</sup> In the recent years, cation exchange reactions have gained much attention when tailoring the structure of semiconductor nanoparticles. The big advantage of these reactions is that they often completely retain the anionic structure of a given nanoobject while the cations are replaced.  $^{12-24}$ 

CdSe@ZnS and CdSe@CdS heterostructures are of interest due to the high photoluminescence (PL) quantum efficiencies because of the type-I like band alignment which effectively confines the charge carriers to the CdSe part of the structure (see band alignment in Scheme 1).<sup>2,3</sup> It is well-known that ZnS is a higher band gap semiconductor than CdS resulting in better confinement of charge carriers in the CdSe core when used as a shell material. However, also the lattice mismatch of ZnS with respect to CdSe is much larger (10.7%) than the lattice mismatch between CdSe and CdS (4.2%) [ICDD, cards no. 00-008-0459 (CdSe, hex), 01-079-2204 (CdS, hex) and 01-077-2306 (ZnS, hex)]. Consequently, CdSe@CdS@ZnS core@ Scheme 1. Reaction Scheme of the Consecutive Ion Exchange and the Relative Alignment of the Band Gaps



shell@shell structures have been proposed as systems with an excellent confinement of the charge carriers and still tolerable lattice mismatches at each interface.<sup>25</sup> To date, such systems exist mainly as spherical particles. Deka et al. have reported an approach yielding CdSe@CdS quantum rods with an ultrathin surrounding layer of ZnS.<sup>26</sup> Here, we demonstrate the synthesis of CdSe@CdS/ZnS heteronanorods with a segmented material structure. Moreover, in our approach we are able to fine-tune the segment border. The synthesis is realized via combining a seed mediated growth approach with a partial ion exchange procedure in which the CdS part of a CdSe@CdS rod is first partially exchanged to Cu<sub>2-x</sub>S, and, subsequently, this Cu<sub>2-x</sub>S part is again exchanged to ZnS. Today's nanoparticle research often involves contacting fluorescent quantum dots or quantum rods by connecting them to e.g. surfaces, metal particles, or other moieties.<sup>27</sup> Depending on the application, a good electronic insulation of the fluorescent part of the quantum dot or quantum rod can be necessary and is usually not sufficiently provided by CdS in a CdSe@CdS nanorod due to the very low conduction band offset between CdS and CdSe (which is much larger between ZnS and CdS/CdSe).

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Accordingly, the CdSe@CdS/ZnS rods with ZnS ends presented here might be of particular interest for all types of applications where such rods shall be connected end-on to some other moiety and where a good insulation of the CdSe core is necessary. It should be emphasized that no direct synthetic pathway to such structures exists today, likely due to the large lattice mismatch between CdS and ZnS, which usually causes heterogeneous nucleation of ZnS.

## RESULTS AND DISCUSSION

Scheme 1 visualizes the ideal structure of the prepared nanoheterostructures together with the relative alignment of the (bulk) band gaps of the respective materials. CdSe@CdS seeded quantum rods undergo a partial and regioselective cation exchange resulting in CdSe@CdS/Cu<sub>2-x</sub>S quantum rods. The resulting rods themselves can undergo a selective cation exchange ultimately resulting in CdSe@CdS/ZnS quantum rods. It is important to note that in the first ion exchange step, an exactly calculated amount of Cu<sup>+</sup> ions is used (see the Experimental Section for details), while in the second step a large excess of Zn<sup>2+</sup> ions is used (more than 3 orders of magnitude Zn excess). The first ion exchange step occurs regioselectively from the tips of the nanorods since this way the interfacial energies between Cu2-xS and CdS can be minimized.<sup>16</sup> The second exchange is regioselective due to the fact that under the given reaction conditions (especially due to the differences in coordination energies for Cu<sup>+</sup> ions and Cd<sup>2+</sup> ions in the used ligand mixture) only Cu<sup>+</sup> ions are replaced by  $Zn^{2+}$ , while  $Cd^{2+}$  ions are not affected in the second step.<sup>28</sup> Note that reference experiments in which pure CdSe@ CdS nanorods were subjected to conditions equal to the second ion exchange step (namely large excess of  $Zn^{2+}$  ions and leaving out the first ion exchange step) did not result in any change of the structure, which clearly shows that a direct exchange from  $Cd^{2+}$  to  $Zn^{2+}$  is not possible. This is also the reason why a large excess of Zn<sup>2+</sup> ions can be used in the second ion exchange step, which furthermore warrants a complete exchange of the  $Cu^+$  ions into  $Zn^{2+}$  ions. We also observed that the optical properties of the obtained CdSe@CdS/ZnS structures were better (especially higher photoluminescence (PL) quantum efficiencies), if the intermediate CdSe@CdS/Cu2-rS particles were not stored for longer times but instead were immediately subjected to the second ion exchange step.

Figure 1 summarizes the transmission electron microscopy (TEM) and X-ray diffraction (XRD) characterization of the original CdSe@CdS sample, as well as of the CdSe@CdS/ZnS sample obtained after the described sequence of two cation exchange steps. According to the used amount of Cu<sup>+</sup> ions in this specific Cd<sup>2+</sup> to Cu<sup>+</sup> ion exchange step (molar ratio Cu<sup>+</sup>:Cd<sup>2+</sup> = 1:1), on average 50% of the Cd<sup>2+</sup> ions should have been replaced by Zn<sup>2+</sup> ions in this CdSe@CdS/ZnS structure (since approximately two Cu<sup>+</sup> ions are required to exchange one Cd<sup>2+</sup> ion).

The survey images of the original CdSe@CdS (Figure 1A) sample and the CdSe@CdS/ZnS sample (Figure 1B) show that neither the length (l) of the rods nor the diameter (d) of the rods has changed significantly during the sequential ion exchange steps ( $l = 35.0 \text{ nm} \pm 7.1 \text{ nm}$  before and  $l = 34.5 \text{ nm} \pm 4.5 \text{ nm}$  after the exchange,  $d = 5.8 \text{ nm} \pm 1.2 \text{ nm}$  before and  $d = 5.7 \text{ nm} \pm 0.9 \text{ nm}$  after the ion exchange. CdSe core diameter is 3.9 nm, see also Supporting Information figure S11 for TEM images and corresponding length and diameter histograms for all three stages of the reaction.). This statement,



**Figure 1.** TEM analysis of CdSe@CdS nanorods (panel A) and CdSe@CdS/ZnS nanorods (panel B) with a HRTEM image of the latter ones (panel C). Panels D and E are FFT analysis of the marked areas in a single CdSe@CdS/ZnS nanorod (left square corresponds to the FFT in panel D, right square to the FFT in panel E). Panel F shows the XRD patterns of the two samples.

however, is based on a statistical evaluation of the particle diameters measured in the middle of the rod and thus does not include possible reductions in diameter at the tips of the rods (which is extremely hard to assess statistically). From the survey images it is apparent that the particles exhibit a more inhomogeneous thickness after the ion exchange, which often results in rods with slightly thinner ends. This inhomogeneous thickness seems to arise mainly after the second ion exchange step (see Supporting Information figure SI1 for survey images of the intermediate sample). Furthermore, the ion exchanged samples seem to show a slightly increased tendency to agglomerate when compared to the original rods. Both effects (agglomeration tendency and inhomogeneous thickness) might be caused either by an etching process during the second ion exchange step or could possibly also be caused by excessive washing steps necessary for TEM grid preparation (the ion exchanged samples usually require more washing steps than the original samples for proper TEM characterization, see the Experimental Section). The HRTEM analysis of a typical CdSe@CdS/ZnS rod is shown in Figure 1C together with selected area fast Fourier transformations (FFT) from two parts of this rod (Figure 1D and 1E). The latter are clearly in good agreement with the predicted structure. Namely, at the end of the rods, the lattice spacing of 3.1 Å corresponds to the spacing of {002}-planes along the c-axis of wurtzite ZnS (3.13 Å) [ICDD, card no. 01-077-2306], while at the center of the rod with a value of 3.3 Å it corresponds to the same planes of wurtzite CdS (3.36 Å) [ICDD, card no. 01-079-2204], indicating a segmented structure of the rods rather than an alloyed structure (which would show an intermediate lattice constant, see also Supporting Information figure SI2 for a magnification of the FFTs). Furthermore, none of the HRTEM

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**Figure 2.** EDX analysis of different nanorod samples. Panel A shows the STEM-HAADF image of several nanorods from a sample which has undergone a 50% ion exchange. The corresponding EDX mapping is shown in the panels B and C. In addition to the distinct CdS and ZnS sections even the CdSe core can be detected. Panel D shows an EDX line scan of a single nanorod of this sample with both sides exchanged to ZnS. Panel E shows the STEM-HAADF image of several nanorods from a sample which has undergone a 20% ion exchange with the corresponding elemental maps in panel F and G. Panel H shows an EDX line scan of a single nanorod of this sample with only one side exchanged to ZnS.

images obtained indicated any sort of twinning or other stacking faults at the CdS/ZnS interface, indicating epitaxial growth. Also the XRD patterns of the CdSe@CdS/ZnS sample show clearly the patterns of wurtzite CdS and wurtzite ZnS (CdSe cannot be detected due to the too low volume fraction within the rods), while the patterns of the original CdSe@CdS rods show only the CdS phase (see Figure 1F). Summarizing, all structural characterization data shown in Figure 1 are in line with the idealized structure shown in Scheme 1.

The energy dispersive X-ray spectroscopy (EDX) line scan measured on a single CdSe@CdS/ZnS nanorod shown in Figure 2D clearly proves the predicted structure of the CdSe@ CdS/ZnS nanorods, revealing a clear border between the Cd containing section and the Zn containing sections. Hence, the presence of a strongly alloyed structure can be safely ruled out (which is also backed up by the optical investigations discussed later).

Within the margins of error, this line scan is also in good agreement with a rate of 50%  $Cd^{2+}$  to  $Zn^{2+}$  exchange, with the elemental analysis of the overall sample via AAS (atomic absorption spectroscopy, see the Supporting Information) and a large area EDX analysis (cation mole fractions of 56% for Zn and 44% of Cd are obtained via EDX analysis of a larger area for this sample) as well as with the used amount of Cu<sup>+</sup> ions in the first ion exchange step (molar ratio  $Cu^+:Cd^{2+} = 1:1$ ). Furthermore, we show color coded elemental mappings of four nanorods recorded via EDX mapping in scanning TEM highangle annular dark-field (STEM-HAADF) mode in Figure 2B and 2C (with Figure 2A being the original STEM-HAADF image). The figure panels 2E, 2F, 2G, and 2H show similar scans as those shown in 2A-D but measuring a sample in which only 20% of  $Cd^{2+}$  ions should be replaced by  $Zn^{2+}$  ions according to the used amount of Cu<sup>+</sup> ions used in the first ion exchange step. These images clearly show that also at a low amount of cation exchange, the exchange occurs selectively at the tips of the rods. Furthermore, these images reveal that we do not only find rods with ZnS compartments on both ends of the rods but also rods with only one ZnS compartment on just one side of the heterostructure especially at lower cation exchange rates (see e.g. the line scan in Figure 2H for a rod

with cation exchange only at one side). This indicates that the initiation of the  $Cd^{2+}$  to  $Cu^+$  ion exchange step has an activation barrier that differs from nanorod to nanorod, as reported by Miszta et al. for octapods.<sup>14</sup> Also for the sample with 20% cation exchange, the large area EDX analysis is in good agreement with the expected structure (cation mole fractions of 24% for Zn and 76% for Cd are obtained via EDX analysis of a larger area for this sample). Summarizing the elemental mapping of individual rods of different samples together with the large area elemental analysis via EDX of these samples allows the conclusion that the segment border between CdS and ZnS can indeed be fine-tuned via the amount of  $Cu^+$  ions used in the first ion exchange step. This finding is furthermore supported by the optical data shown below.

In Figure 3 we show a series of absorption spectra of CdSe@ CdS rods which have been subjected to partial cation exchange reactions with various ratios reaching from 0% up to 100%  $Cd^{2+}$  to  $Zn^{2+}$  ion exchange in steps of 20%. Here, it should be clarified that the numbers for the  $Zn^{2+}$  cation mole fraction



**Figure 3.** Absorption spectra of nanorods with different Zn:Cd ratios. The ZnS band is seen at 320 nm and the CdS band is seen at 470 nm. The insets show magnifications of the absorption of the CdSe core (620 nm) and the ZnSe core (400 nm).

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given in the figure (Zn:(Zn+Cd)) and in all following figures relates to the mole fraction expected in this structures according to the mechanism shown in Scheme 1 (and not to the ratio used in the synthesis). During the synthesis, only the Cd<sup>2+</sup> to Cu<sup>+</sup> ion exchange step is done using a calculated amount of Cu<sup>+</sup>:Cd<sup>2+</sup>, while in the Cu<sup>+</sup> to Zn<sup>2+</sup> ion exchange step Cu<sup>+</sup> is quantitatively replaced using an excess of Zn<sup>2+</sup> ions, however leaving the  $Cd^{2+}$  ions untouched in this step. As expected, the absorption spectrum of the original CdSe@CdS rods shows an absorption maximum at around 625 nm, which can be assigned to the CdSe core of the particles (see lower inset), and a characteristic shoulder at 470 nm, belonging to the CdS body of the rods. Analogous, the spectrum of the 100% cation exchanged sample shows a small maximum at 403 nm belonging to the ZnSe core (see upper inset) and a shoulder at 315 nm belonging to the ZnS body of the rod. Thus, after complete ion exchange, we have obtained ZnSe@ZnS quantum rods as already shown by Li et al.<sup>28</sup> More peculiar are the absorption spectra in between these two extremes. Interestingly, the spectra of the partially exchanged systems show almost no smooth shifting of the absorption edge of the CdS toward the one of the ZnS which would point to the presence of an (partially) alloyed structure. It is known that the band gap of Zn<sub>1-x</sub>Cd<sub>x</sub>S nanoparticles shifts almost linearly between the two values of the pure phases.<sup>29</sup> Instead, we find that the absorption at the position of the CdS band edge (around 470 nm) decreases when more cations are exchanged, while simultaneously the absorption at the position of the ZnS band edge (around 320 nm) increases. This finding matches very well our proposed mechanism as shown in Scheme 1.

Yet another indication for the fact that Cu<sup>+</sup> is completely exchanged by  $Zn^{2+}$  in the second ion exchange step is the fact that the presence of even smallest amounts of Cu<sup>+</sup> ions in the CdSe@CdS quantum rods would have resulted in almost complete quenching of the fluorescence of the rods. For example, with a Cu:Cd ratio of 0.01 in the first exchange step, the quantum yield of the nanorods decreased already from 44.5 to 6.4%, and with a ratio of 0.1 it decreased to 0.2% (see Supporting Information figure SI8). Instead, the CdSe@CdS/ ZnS quantum rods obtained after the second ion exchange step are again quite strong emitters. Even though the quantum yields of the original CdSe@CdS rods are usually not completely recovered, the CdSe@CdS/ZnS can easily reach quantum yields of 20% or higher again giving strong evidence that the Cu<sup>+</sup> ions are quantitatively removed in the second ion exchange step.

The corresponding emission spectra of the samples (Figure 4) show that for cation exchange up to 40% only the emission band from the CdSe core is observed, which is a clear hint that up to this ratio the majority of CdSe cores remains unaffected by the cation exchange procedure (apart from a very small blue shift which is possibly caused by a slightly shrinking diameter close to the seed position in some rods). The emission quantum yield is 34% for the starting material which decreases to 17% for 40% cation exchange and decreases even further for higher Zn:Cd ratios. Additionally, at higher exchange ratios, the emission spectra become more and more complicated, which can be explained easily by the fact that not only the CdS is converted to ZnS but also the CdSe core is partially or in some rods also completely converted to ZnSe giving rise to a large variety of different heterostructures in the particle ensemble depending on the progress of the exchange on each individual nanorod. Therefore, we would assign the broad emission signal

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Figure 4. Fluorescence emission spectra of nanorods with different Zn:Cd ratios.

between 450 and 550 nm occurring especially in the samples with Zn:(Zn+Cd) = 0.6 and Zn:(Zn+Cd) = 0.8 to emission originating from particles which have undergone already an almost complete ion exchange from  $Cd^{2+}$  ion to  $Zn^{2+}$  but which still contain some  $Cd^{2+}$  ions in the core of the seeded rod (hence containing a  $Zn_xCd_{1-x}Se$  core with a band gap energy between the band gap energy of ZnSe and the one of CdSe).

Figure 5 shows absorption and emission spectra of the original CdSe@CdS sample as well as of the CdSe@CdS/ZnS



**Figure 5.** Panel A shows absorption (solid lines) and emission (dotted lines) spectra of CdSe@CdS nanorods compared to CdSe@CdS/ZnS nanorods with a Zn:(Zn+Cd) ratio of 0.4. The emission was measured at an excitation wavelength of 475 nm. Panel B shows fluorescence excitation spectra of the same samples measured at an emission wavelength of 635 nm.

sample (after 40% cation exchange and thus mostly intact CdSe cores) (panel A) together with the fluorescence excitation spectra of the respective samples recorded at an emission wavelength of 635 nm (panel B). These spectra demonstrate that also high energetic excitation of the formed nanoheterostructure (which is expected to yield excitons delocalized over the whole particle as long as the excitation energy is higher than the ZnS band gap) results in an emission from the CdSe core of the heterostructure with a high efficiency. By dividing the excitation spectra by the absorption spectra, the quantum efficiencies at various excitation wavelengths can be extracted (see Supporting Information figure SI9). Although there is a continuous decline in quantum yield at lower excitation

wavelengths (which is observed also for the CdSe@CdS rods but a little less pronounced), no sudden drop of the quantum yield is observed once the band gap energy of ZnS is reached (wavelength below 330 nm). This finding can be interpreted in a way that the CdSe@CdS/ZnS samples do not only absorb relatively more light in the high energetic part of the spectrum but that this higher absorption also leads to a stronger emission of light from the CdSe core, even though some new nonradiative channels seem to exist for high energetic excitation. In other words, the charge carrier relaxation seems to be still efficient also from the ZnS compartment through the CdS compartment to the CdSe core, which indirectly indicates that there are no larger potential barriers between these compartments (like e.g. cracks or twinning planes). Summarizing the steady state optical data, one can conclude, that up to cation exchange of 40%, the heterostructures obtained via the sequential ion exchange have still a more or less unaffected CdSe core which dominates the emission behavior of the overall structure.

Figure 6 shows fluorescence decay measurements of the original CdSe@CdS rods as well as of the obtained CdSe@



Figure 6. Fluorescence decay of nanorods with different Zn:Cd-ratios. The emission decay was measured at 635 nm for all samples except Zn:(Zn+Cd) = 1.0, which was measured at 405 nm.

CdS/ZnS rods. It can be observed that the measured decay times are getting shorter with an increased fraction of ZnS. Especially for the samples with higher amounts of ZnS (Zn:(Zn +Cd) = 0.6 and Zn:(Zn+Cd) = 0.8) the decay behavior is clearly more polyexponential than for those samples with either a very low or very high Zn:Cd ratio. Again this likely indicates the presence of nanorods in these samples in which the CdSe core is partially or even completely affected by the Cd<sup>2+</sup> to Zn<sup>2+</sup> ion exchange procedure. For less than 40% cation exchange, we find more monoexponential behavior with comparable decay constants at least at the beginning of the decay process. The slight shortening of the fluorescence lifetime from 25 ns for CdSe@CdS rods to 20 ns for CdSe@CdS/ZnS rods with a molar ratio of Zn:(Zn+Cd) = 0.4 is in line with the observed decrease in fluorescence quantum yield. It indicates a slight increase in nonradiative decay channels with increasing amounts of ZnS in the structure. Thus, the lifetime measurements confirm that the main radiative process in the obtained CdSe@CdS/ZnS rods is similar to the one in CdSe@CdS nanorods, namely the recombination within the CdSe core,

even though the decay behavior becomes more polyexponential with higher amount of ZnS.

Summarizing, we have shown the first synthetic pathway toward CdSe@CdS/ZnS nanorods with a sharp boundary between the CdS and the ZnS part of the rods. TEM as well as optical findings are in very good agreement with an epitaxial and relatively sharp boundary between the two materials. The concept of sequential cation exchange reaction has thus been extended to another interesting material combination which was not accessible via direct synthesis before. Due to the much higher band gap of ZnS, the obtained CdSe@CdS/ZnS structures are interesting alternatives for the much more common CdSe@CdS structures in such application where a good electronic insulation of the CdSe core is necessary and where the nanorods are contacted at the tips of the rods.

# EXPERIMENTAL SECTION

**Chemical List.** Cadmium oxide (CdO, 99.98%), selenium (Se, 99.999%, 200 mesh), and methanol (MeOH, 99.9%, anhydrous) were purchased from Alfa Aesar. Hydrochloric acid (HCl, 37%), nitric acid (HNO<sub>3</sub>, >69%), sulfur (S, 99.98%), tetrakis (acetonitrile)copper(I) hexafluorophosphate ([Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, 97%), toluene (99.8%, anhydrous), and zinc chloride (ZnCl<sub>2</sub>, 99.999%) were purchased from Sigma-Aldrich. Tri-n-octylphosphine (TOP, 97%) and tri-n-octylphosphine oxide (TOPO, 99%) were purchased from ABCR. Octadecylphosphonic acid (ODPA, >99%) and hexylphosphonic acid (HPA, >99%) were purchased from PCI Synthesis. 1-Octadecene (ODE, 90%) and oleylamine (OLAM, 80–90%) were purchased from Acros Organics. Ethanol (absolute, <0.01% H<sub>2</sub>O) was purchased from Merck Chemicals. Rhodamine 6G was purchased from Lambda Physik. Toluene and hexane for spectroscopy were both purchased from Roth in UV/IR grade.

Synthesis of CdSe Seeds. CdSe quantum dots were synthesized similar to the procedure of Carbone et al.<sup>7</sup> CdO (0.060 g), TOPO (3.0 g), and ODPA (0.280 g) were degassed under vacuum at 100 °C for 1 h. The mixture was heated up to 300 °C under nitrogen atmosphere, and 1.8 mL of TOP was injected. The mixture was then heated up to 380 °C. To this mixture, a solution of 1.8 mL of TOP and 0.058 g of Se which was prepared under argon was injected. The reaction was quenched quickly after 20 s by injection of 5 mL of TOP and use of a water bath, and after a sufficient decrease in temperature by the addition of 10 mL of toluene. The obtained quantum dots were precipitated by adding an excess of methanol and centrifugation at 3843 g. The quantum dots were redispersed in toluene for storage. Samples of this solution were dried under a nitrogen flow and redispersed in UV/IR grade toluene for optical characterization and to determine the concentration by means of empirical equations presented by Yu et al.<sup>30</sup>

**Synthesis of CdSe@CdS Nanorods.** CdSe@CdS nanorods were synthesized similar to the procedure of Carbone et al.<sup>7</sup> CdO (0.060 g), TOPO (3.0 g), ODPA (0.290 g), and HPA (0.080 g) were degassed under vacuum at 100 °C for 1 h. The mixture was heated up to 300 °C under nitrogen atmosphere, and 1.8 mL of TOP was injected. The mixture was then heated up to 350 °C. To this mixture, a solution of 8  $\mu$ mol of CdSe dispersed in a 2 M TOP:S solution (1.8 mL TOP:0.120 g S) was injected. The reaction was quenched after 8 min. After a sufficient temperature decrease, 10 mL of toluene was added to the mixture. The acquired CdSe@CdS nanorods were precipitated by adding an excess of methanol and centrifuged at 3843 g. The nanoparticles were redispersed in 2 mL of toluene under argon for further steps.

Synthesis of CdSe@CdS/Cu<sub>2-x</sub>S Rods.  $CdSe@CdS/Cu_{2-x}S$  rods were synthesized adapting the procedure introduced by Li et al.<sup>9</sup> by varying the amount of Cu precursor used. The Cd concentration of the obtained CdSe@CdS nanorod solution was determined by atomic absorption spectroscopy (AAS). A stock solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]-PF<sub>6</sub> in methanol was prepared under inert conditions with a concentration being five times lower than the Cd<sup>2+</sup> concentration of the above-described solution of CdSe@CdS nanorods. This [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> stock solution was used to produce solutions with different Cu<sup>+</sup> concentrations by diluting 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 mL of this solution up to 1 mL with methanol. Subsequently, 100  $\mu$ L of the CdSe@CdS nanorod solution was diluted with toluene to yield a volume of 2 mL. For each cation exchange experiment, 1 mL of the differently concentrated [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> solutions was added to 2 mL of the diluted CdSe@CdS nanorod solution under stirring in inert conditions. This way, the Cu:Cd ratio was varied from 0.4 to 2 (keeping in mind that approximately two Cu<sup>+</sup> ions replace one  $Cd^{2+}$  ion, this corresponds to 20% up to 100% exchange of the original Cd<sup>2+</sup> ions). After 5 min the mixture was separated in a centrifuge at 3461 g. The solvents were removed keeping inert conditions. The obtained CdSe@CdS/Cu<sub>2-x</sub>S rods were then redispersed in 0.2 mL of toluene and 2 mL of TOP, and the rod solution was immediately subjected to the Cu<sup>+</sup> to Zn<sup>2+</sup> ion exchange step described below.

Synthesis of CdSe@CdS/ZnS Nanorods. CdSe@CdS/ZnS nanorods were synthesized adapting the procedure of Li et al.<sup>28</sup> but using CdSe@CdS/Cu<sub>2-x</sub>S rods as the starting material. ZnCl<sub>2</sub> (0.2627 g), ODE (6 mL), and OLAM (4 mL) were degassed under vacuum at 100 °C for 1 h and then heated to 250 °C under nitrogen atmosphere. At this temperature, the complete batch of obtained CdSe@CdS/Cu<sub>2-x</sub>S rods solution was injected into the mixture, and the reaction was carried out for 3 min. Subsequently, the mixture was cooled down rapidly using a water bath.

The nanorods were precipitated by adding 5 mL of toluene and 15 mL of methanol and subsequent centrifugation at 3843 g. Afterward the nanoparticles were redispersed in either toluene or hexane for optical characterization and storage.

**TEM and STEM Analysis.** TEM and HRTEM measurements were conducted using a FEI Tecnai G2 F20, equipped with a field emission gun operated at 200 kV.

HRTEM, STEM-HAADF, and EDX measurements were conducted using a JEOL JEM-2100F, equipped with a field emission gun operated at 200 kV. Elemental analysis was performed by EDX analysis in STEM mode.

Samples have been prepared by placing a QUANTIFOIL carbon coated copper grid (300 mesh) on a filter paper and dropping  $10 \,\mu$ L of a thoroughly washed and highly diluted particle solution on it. It should be pointed out that after each cation exchange step, the samples needed to be washed significantly more times in order to avoid carbon contamination upon electron irradiation during electron microscopy.

**Optical Spectroscopy.** UV/vis absorption spectra were recorded using an Agilent Cary 5000 absorption spectrophotometer. All spectra were recorded in 1 cm quartz cuvettes using hexane as solvent (UV/vis spectroscopy grade).

Emission spectra were recorded using a Horiba Fluoromax-4 emission spectrophotometer. All spectra were recorded in 1 cm quartz cuvettes using hexane as solvent (UV/vis spectroscopy grade). Emission lifetime spectroscopy was performed with the same Fluoromax-4 spectrophotometer with an additional time correlated single photon counting (TCSPC) accessory and ns pulsed LEDs as excitation source (full width at half-maximum of the pulse ~1.2 ns, wavelength of the pulse 255 nm, 368 nm, or 454 nm).

**X-ray Diffraction.** X-ray diffraction was carried out using a Bruker D8 Advance in reflection mode. The samples were prepared by dropcasting and drying a concentrated nanorod/toluene solution onto a single crystal silicon carrier.

**Elemental Analysis.** Quantitative elemental analysis (cadmium) was determined by atomic absorption spectroscopy using a Varian AA 140 spectrometer. For this purpose the samples were dissolved with aqua regia and diluted with deionized water. The measurements were carried out with a wavelength of 228.8 nm and an acetylene/air flame. For the calculation of the cadmium concentration, cadmium calibration solutions were used.

# ASSOCIATED CONTENT

## **S** Supporting Information

TEM images, length and diameter histograms of CdSe@CdS, CdSe@CdS/Cu<sub>2-x</sub>S and of CdSe@CdS/ZnS nanorods. Additional TEM characterization (enlarged FFTs, additional EDX analysis). AAS analysis of the Cd content of the CdSe@CdS/ ZnS structures. Fluorescence and absorption spectra of several samples after the Cu<sup>+</sup> ion exchange step. Fluorescence decay measurements at different excitation wavelengths. Quantum yield and fluorescence decay of various CdSe@CdS and CdSe@CdS/ZnS rods. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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