

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

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Abstract

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) are realized exploiting a sequential cation exchange mechanism. In a first step, CdSe@CdS rods are transformed into CdSe@CdS/Cu_{2-x}S rods. In a second step, the latter ones are converted into CdSe@CdS/ZnS rods. By varying the amount of Cu⁺ precursor in the Cd²⁺ to Cu⁺ 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.

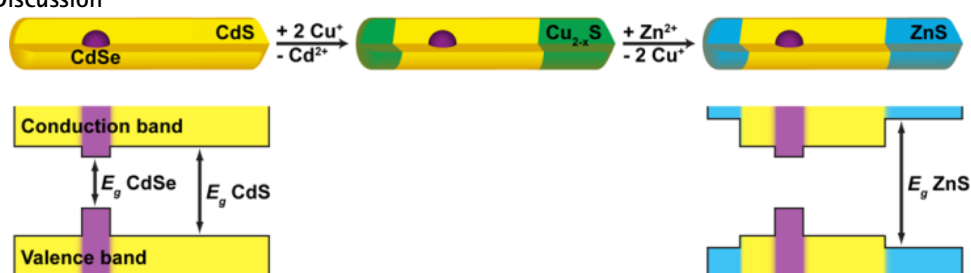
Introduction and Motivation

Nowadays, semiconductor nanoparticles are a well-known material class. By means of the hot-injection synthesis a large variety of particles and heteroparticles is accessible with high shape and composition control.¹ Recently, cation exchange reactions gain more and more attention as a way to change the composition of a synthesized particle while retaining the shape.²

CdSe@CdS and CdSe@ZnS are an interesting group of heterostructures due to their high photoluminescence quantum efficiencies.³ CdSe has a low band gap energy compared to CdS and even lower compared to ZnS. This leads to a confinement of the charge carriers in the CdSe part of the structure. However the lattice mismatch between CdSe and ZnS does not allow a direct growth of ZnS on CdSe particles.⁴ By means of a sequential cation exchange however, we were able to convert easily accessible CdSe@CdS seeded nanorods to CdSe@CdS/ZnS nanorods where the CdS and ZnS phases share a clear boundary. Moreover, we were able to fine tune the segment border.

A good electronic insulation of the fluorescent part of the nanorod is preferable but unfortunately this is not provided by CdS due to the very low conduction band offset. However, ZnS has a much higher conduction band offset, therefore providing the requested insulation. This could prove useful in future applications where a contact between the fluorescent nanoparticles and metal particles or other surfaces has to be established while separating the charge carriers.⁵

Results and Discussion



Scheme 1: Reaction scheme of the consecutive ion exchange and the relative alignment of the band gaps. (Reprinted with permission from Adel et al.: *Chem. Mater.* 2014, 26, 10, 3121–3127. Copyright © 2014 American Chemical Society.)

Scheme 1 shows the reaction sequence which leads to segmented CdSe@CdS/ZnS nanorods in two consecutive steps. In the first step parts of CdSe@CdS nanorods are exchanged to Cu_{2-x}S, leading to segmented CdSe@CdS/Cu_{2-x}S nanorods. This is realized by adding calculated amounts of a Cu⁺ precursor to the CdSe@CdS nanorods. The second step is carried out directly afterwards by exchanging the Cu⁺ ions to Zn²⁺ using a large excess of Zn²⁺ therefore obtaining ZnS parts. A direct exchange from Cd²⁺ to Zn²⁺ does not occur at any given time during the reactions.⁶

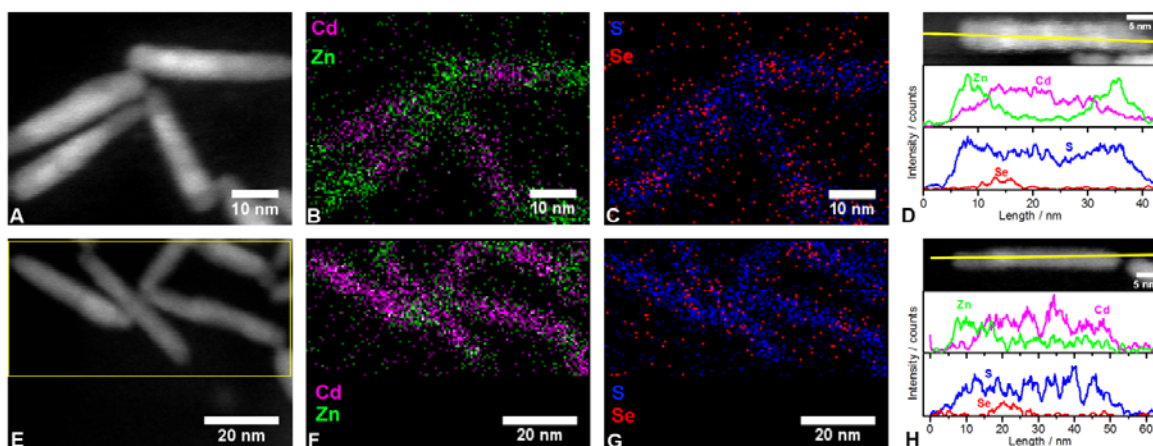


Figure 1: EDX analysis of different nanorod samples. Panel A shows the STEM-HAADF image of several nanorods from a sample which has undergone a 50 % ion exchange. The corresponding EDX mapping is shown in the panels B and C. In addition to the distinct CdS and ZnS sections even the CdSe core can be detected. 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. (Reprinted with permission from ADEL ET AL.: *Chem. Mater.* 2014, 26, 10, 3121–3127. Copyright © 2014 American Chemical Society.)

Figure 1D shows the energy dispersive X-ray spectroscopy (EDX) line scan of CdSe@CdS/ZnS nanorods with 50 % of the Cd²⁺ exchanged to Zn²⁺. This proves the predicted structure as shown in Scheme 1 by revealing a clear border between the CdS and the ZnS part of the nanorod. Alloying can be safely ruled out by this finding. In Figure 1H a similar line scan is shown of a CdSe@CdS/ZnS nanorod with only 20 % of the Cd²⁺ exchanged to Zn²⁺. When compared to Figure 1D, the tunability of the border is clearly visible. Figures 1A–C show color coded elemental mapping of CdSe@CdS/ZnS nanorods with 50 % cation exchange. In addition to the clear borders between CdS and ZnS the CdSe cores were also detectable. Figures 1E–G show similar elemental mappings of CdSe@CdS/ZnS nanorods with 20 % cation exchange. Again the noticeably smaller ZnS parts show the tunability of the border between CdS and ZnS.

Conclusion

We have shown the first synthetic pathway towards CdSe@CdS/ZnS nanorods with a sharp boundary between the CdS and the ZnS parts of the rods. The concept of sequential cation exchange reactions has been herewith extended to another interesting material combination which was not directly accessible. These new types of nanorods are promising candidates for applications where a good electronic insulation of the CdSe core is necessary and where the nanorods are contacted end-on.

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