Electronic Supplementary Information (ESI)

Heat-induced transformation of CdSe/CdS/ZnS core/multishell quantum dots by Zn diffusion into inner layers

Anil O. Yalcin,*[a] Bart Goris,[b] Relinde J. A. van Dijk - Moes,[c] Zhaochuan Fan,[d] Ahmet K. Erdamar,[a] Frans D. Tichelaar,[a] Thijs J. H. Vlugt,[d] Gustaaf Van Tendeloo,[b] Sara Bals,[b] Daniël Vanmaekelbergh,[c] Henny W. Zandbergen[a] and Marijn A. van Huis[e]

[a] *Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands.*
E-mail:a.o.yalcin@tudelft.nl
[b] *Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.*
[c] *Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands.*
[d] *Process and Energy Laboratory, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands.*
[e] *Debye Institute for Nanomaterials Science, Center for Extreme Matter and Emergent Phenomena, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands.*

Electronic Supplementary Information Contents:

A. Supplementary movies

- In general, a heating rate of 10 degrees/min was used.

Movie S1: Thermal annealing of CdSe/CdS/ZnS core/multishell QDs from 200 ^{0}C to 320 ^{0}C in low resolution. The movie is accelerated 15 times.

Movie S2: Partial sublimation of a single CdSe/CdS/ZnS core/multishell QD (**Fig. 3** in the main text) at 310 ^{0}C. The movie is accelerated 15 times.

B. CdSe/CdS/ZnS core/multishell QD synthesis method

All nanocrystals syntheses were performed in a nitrogen atmosphere and stored in a glovebox and with pre-dried chemicals.

*Chemicals***.** $Cd(Ac)_2$ (Sigma-Aldrich, 99%), diethylzinc (Et_2Zn, Sigma-Aldrich, 1.0 M solution in hexane), Oleic acid (OA, Sigma-Aldrich, 90%), octadecene (ODE, Sigma-Aldrich, 90%), octadecene amine (ODA, Sigma-Aldrich, 90%) selenium (Strem Chemicals, 99.99%), sulphur (Alfa Aesar, 99%), trioctylphosphine (TOP, Sigma-Aldrich, 90%), trioctylphosphine oxide (TOPO, Sigma-Aldrich, 99%), were used for the synthesis of QDs.

*Solvents***.** Acetone (Merck), cyclohexane (Sigma-Aldrich, anhydrous, 99%), hexane (Sigma-Aldrich, anhydrous, 99.8%), methanol (Sigma-Aldrich, anhydrous, 99.8%), toluene (Sigma-Aldrich, anhydrous, 99.8%)

*Synthesis of CdSe QD seeds***.**[1] Prior to the synthesis of the CdSe QDs, 2 precursors were synthesized. OA (3.68 g), ODE (25.92 g), and $Cd(Ac)_2$ (0.64 g) were mixed, heated to 150°C, and kept under vacuum for 2 h to form $Cd(OA)_2$. Selenium (4.25 g) was dissolved in TOP (22.5 g) at 50 °C, followed by the addition of ODE (35.7 g).
CdSe nanocrystal seeds were synthesized in 50 ml three-neck flask using a Schlenk-line. TOPO (1.11 g), ODA (3.20 g), and $Cd(OA)_2$-precursor (4.9 g) were mixed, heated to 300 °C. When this temperature was reached, the Se-precursor (5.2 g) was added rapidly. The size of the QDs can be tuned via changing the reaction time.
The particles were diluted by adding 1 equivalent of hexane. The QDs were washed by adding 2 equivalents of methanol and collecting the upper hexane layer (coloured) and add 1 equivalent of acetone to precipitate the QDs. Finally, the nanocrystal seeds were re-dissolved in toluene and stored inside a glove box under nitrogen atmosphere.

*Typical synthesis of CdSe/CdS/ZnS QDs***.**[2] Prior to the synthesis of the CdSe QDs, three precursors were prepared. The zinc precursor solution (0.1 M) was prepared by dissolving $Zn(Et)_2$ (0.494 g) in oleic acid (5.05 mL) and ODE (19.8 mL) at 310 °C. The cadmium precursor solution (0.1 M) was prepared by dissolving $Cd(Ac)_2$ (1.10 g) in oleic acid (10.83 g) and ODE (43.20 mL) at 120 °C under vacuum for 2 h. The sulphur precursor solution (0.1 M) was prepared by dissolving sulphur (0.032 g) in ODE (10 mL) at 180 °C. The Cd-, and Zn-precursor Cd/Zn-precursor solutions were kept at about 80 °C, while the sulphur injection solution was allowed to cool to room temperature. For each shell growth, a calculated amount of a given precursor solution was injected with a syringe using standard air-free procedures. CdSe QDs ($1 \cdot 10^{-7}$M of 2.91 nm QDs), ODE (5.0 g) and ODA (1.5 g) were combined and heated up to 150 °C for 1 h to remove all toluene. The reaction temperature was increased to

240 °C and in steps with reaction periods of 30 minutes and precursors were added slowly to grow the cell half-monolayer by half-layer. Table S1 below summarizes each step of the shell growth process.

Table S1. Stepwise explanation of shell growth on CdSe QD seeds.

Step	Total # monolayers	Added Precursors	Amount (µL)
1	0.5	Cd + S	105
2	1	Cd + S	125
3	1.5	Cd + S	150
4	2	Cd + S	180
5	2.5	Cd + S	205
6	3	Cd + S	240
7	3.5	Cd + S	270
8	4	Cd + S	305
9	4.5	CdZn + S	345
10	5	CdZn + S	385
11	5.5	Zn + S	430
12	6	Zn + S	475

Following the synthesis of QDs, the reaction mixture was cooled to room temperature and diluted by adding 1 equivalent of hexane. The QDs were washed by adding 2 equivalents of methanol and collecting the upper hexane layer (coloured) and add 1 equivalent of acetone to precipitate the QDs. Finally, the nanocrystal seeds were re-dissolved in cyclohexane and stored inside a glove box under nitrogen atmosphere.

C. Additional Chemi-STEM maps and elemental quantifications

- All elemental quantifications were performed using the Cliff-Lorimer method with k-factors as implemented in the Bruker ESPRIT software.

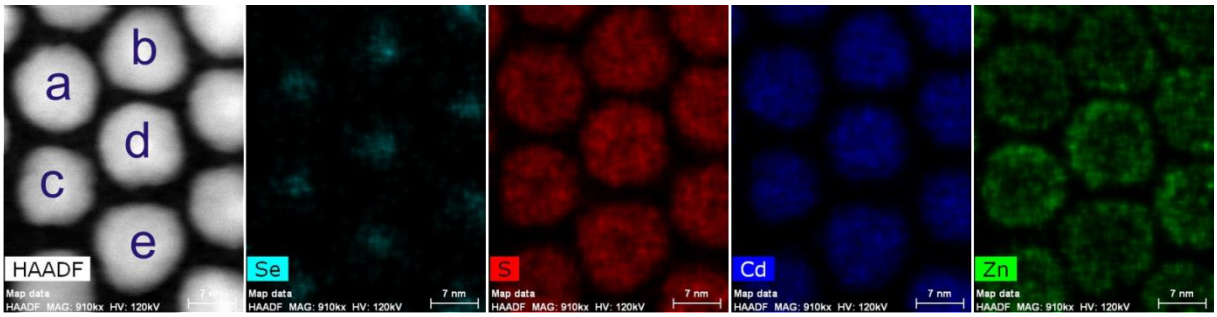

Fig. S1 CdSe/CdS/ZnS core/multishell QDs at initial state. Marked QDs were used for elemental quantification.

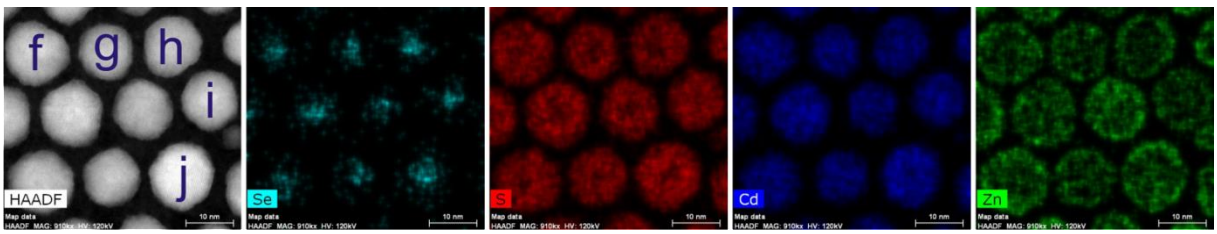

Fig. S2 CdSe/CdS/ZnS core/multishell QDs at initial state. Marked QDs were used for elemental quantification.

Table S2. Elemental quantifications of QDs at initial state depicted with the letters (a-j) in Fig. S1 and S2.

	Atomic percentages				
	Zn	**S**	**Cd**	**Se**	**cation/anion**
a	11.07	45.39	41.13	2.41	1.09
b	10.57	46.59	39.39	3.45	0.99
c	18.74	46.35	32.91	2.00	1.06
d	14.66	47.91	34.94	2.49	0.98
e	11.18	48.81	37.83	2.17	0.96
f	10.86	48.87	37.83	2.44	0.94
g	10.65	48.85	37.64	2.86	0.93
h	9.68	46.70	40.65	2.98	1.01
i	8.70	49.25	39.69	2.35	0.93
j	10.85	46.41	39.49	3.25	1.01
Average	11.69	47.51	38.15	2.64	0.99
Std. Dev.	2.90	1.37	2.56	0.47	0.05

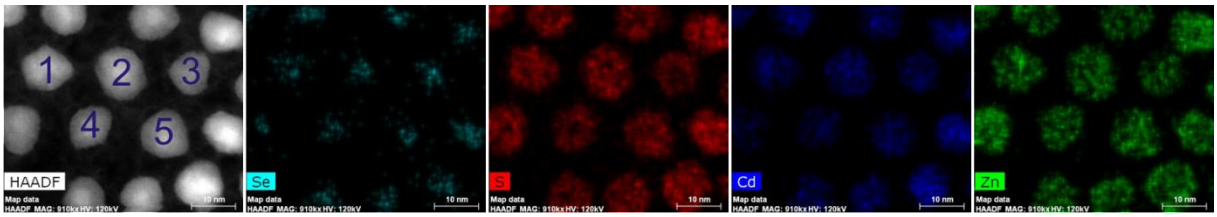

Fig. S3 QDs at heated state ($Cd_xZn_{1-x}Se/Cd_yZn_{1-y}S$ core/shell QDs). Marked QDs were used for elemental quantification.

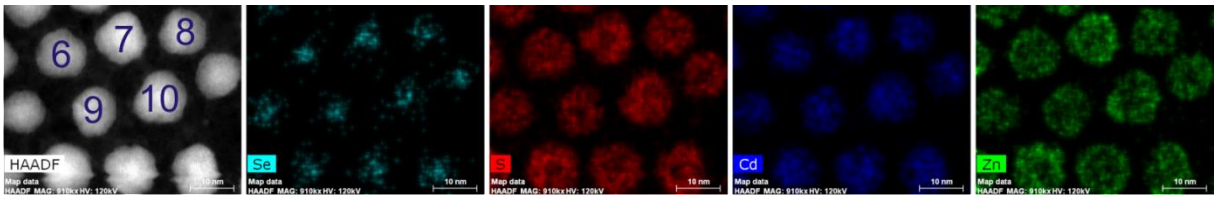

Fig. S4 QDs at heated state ($Cd_xZn_{1-x}Se/Cd_yZn_{1-y}S$ core/shell QDs). Marked QDs were used for elemental quantification.

Table S3. Elemental quantifications of QDs at heated state depicted with the numbers (1-10) in Fig. S3 and S4.

	Atomic percentages				
	Zn	**S**	**Cd**	**Se**	**cation/anion**
1	23.91	49.91	21.72	4.46	0.83
2	22.97	48.22	24.70	4.12	0.91
3	27.38	46.61	21.98	4.03	0.97
4	28.16	46.44	21.75	3.65	0.99
5	20.96	44.30	25.44	9.30	0.86
6	19.84	48.91	27.24	4.01	0.88
7	22.90	44.48	28.17	4.45	1.04
8	19.24	46.82	30.18	3.76	0.97
9	17.59	42.90	34.68	4.82	1.09
10	18.82	46.32	31.43	3.43	1.01
Average	22.17	46.49	26.72	4.60	0.96
Std. Dev.	3.57	2.17	4.44	1.70	0.08

References

1. X. Peng, M. C. Schlamp, A. V. Kadavanich and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1997, **119**, 7019.
2. R. Xie, U. Kolb, J. Li, T. Basché and A. Mews, *J. Am. Chem. Soc.*, 2005, **127**, 7480.