

Supporting information for

Core/shell colloidal semiconductor nanoplatelets

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CdSe/ZnS core/shell nanoplatelets with TMS₂S as sulfide precursor

Synthesis protocol:

400 μ L of the as-synthesized nanoplatelets in hexane were diluted in 2 mL hexane. In a glovebox, 100 μ L of Bis(trimethylsilyl) sulfide (TMS₂S) was introduced into the yellow solution of platelets and let to react for 1 hour. The color of the solution quickly shift from yellow to orange and the platelets began to aggregate with each other, troubling the solution. The resulting nanocrystals were washed 2 times with ethanol and dispersed in hexane. Because of the lack of ligands, the nanocrystals were aggregated. 30 mg of Zn(OAc)₂(H₂O)₂ was then added and the mixture sonicated for 10 minutes, inducing another color change from orange to red. Adding 200 μ L of oleic acid induce the disaggregation of the core/shell platelets and the formation a clear red colored solution.

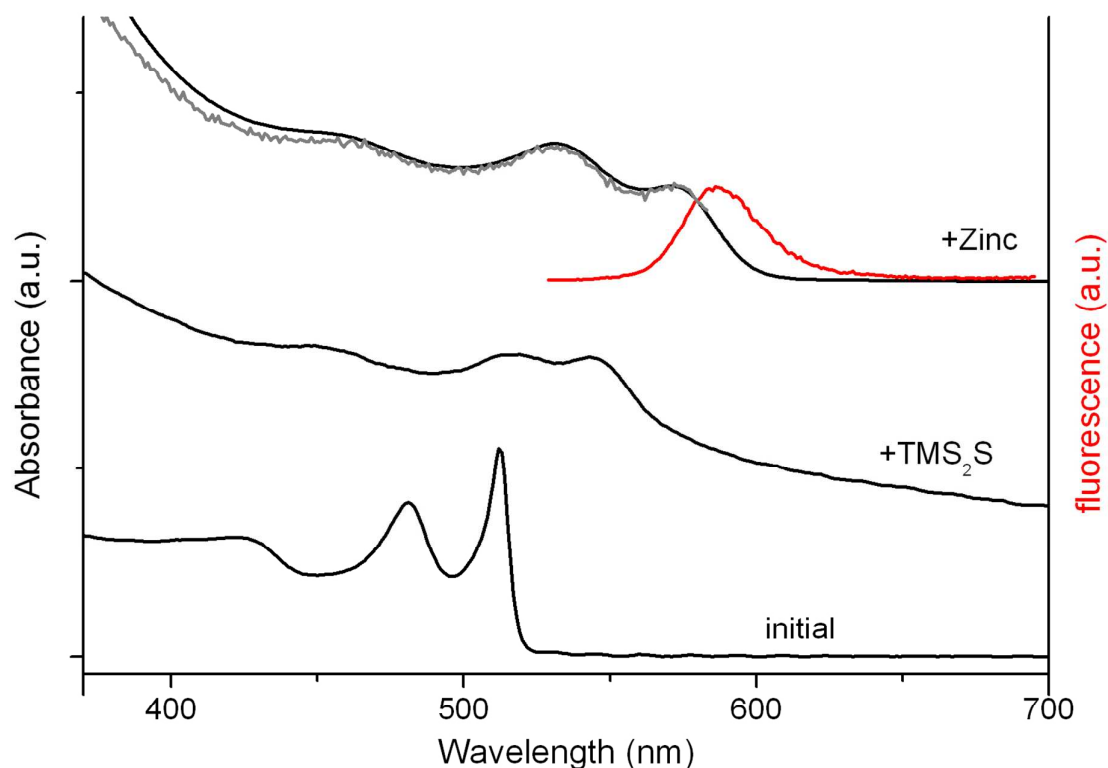


Figure S1: Absorbance (black) spectra of the original CdSe NPLs (up), and after one S²⁻ monolayer deposition (middle) and absorbance (black), fluorescence (red), and photoluminescence excitation (PLE, gray) spectra of CdSe nanoplatelets after one S²⁻ and one Cd²⁺ monolayer deposition (down).

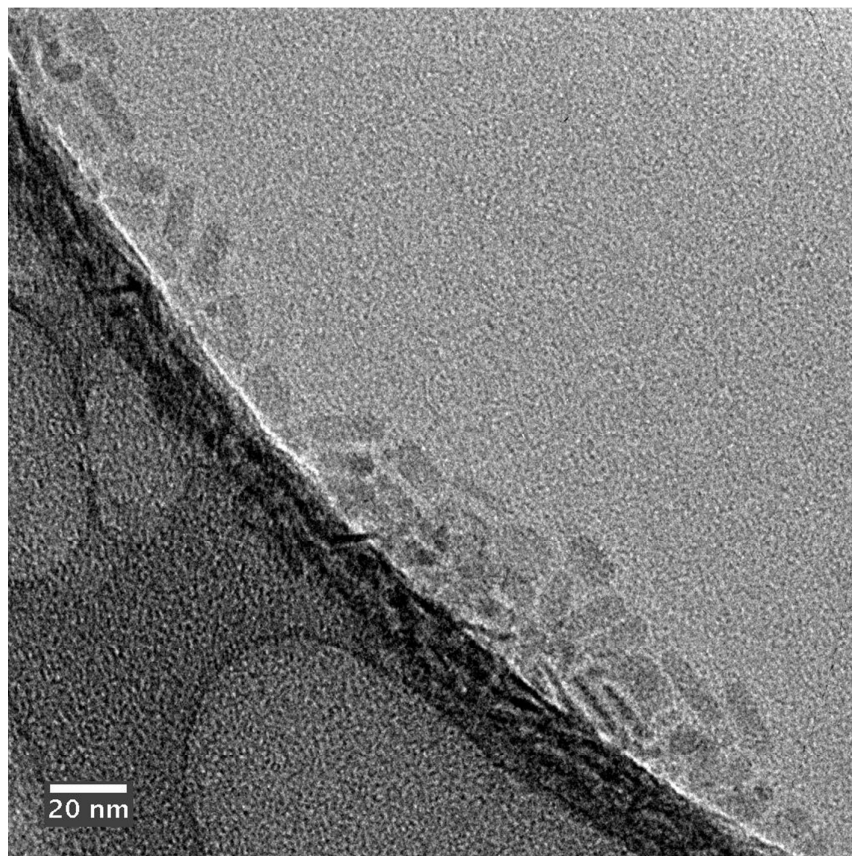


Figure S2: TEM picture of the final CdSe/ZnS core/shell nanoplatelets.

Tetramethyl ammonium sulfide as a sulfide source

Synthesis protocol:

400 μL of the as-synthesized nanoplatelets in hexane were diluted in 2 mL Chloroform and 2 mL of an aqueous solution of tetramethylammonium hydroxide at 100 mg/mL is added in the flask. 100 μL of an aqueous solution of ammonium sulfide (20 %) is swiftly injected into the biphasic mixture. The color of the organic phase (containing the nanoplatelets) instantly shifts from yellow to orange. Under stirring, the platelets are transferred in a few minutes into the upper aqueous phase. Adding 10 mL ethanol transforms the biphasic mixture into a monophasic one and induces aggregation. The platelets are then precipitated by centrifugation and suspended in deionized water. 20 mg of $\text{Cd}(\text{OAc})_2(\text{H}_2\text{O})_2$ are added into the aqueous solution, inducing an immediate color change from orange to deep red and the aggregation of the platelets. After centrifugation, the resulting CdSe/CdS core/shell platelets are suspending into hexane with the help of 200 μL oleic acid.

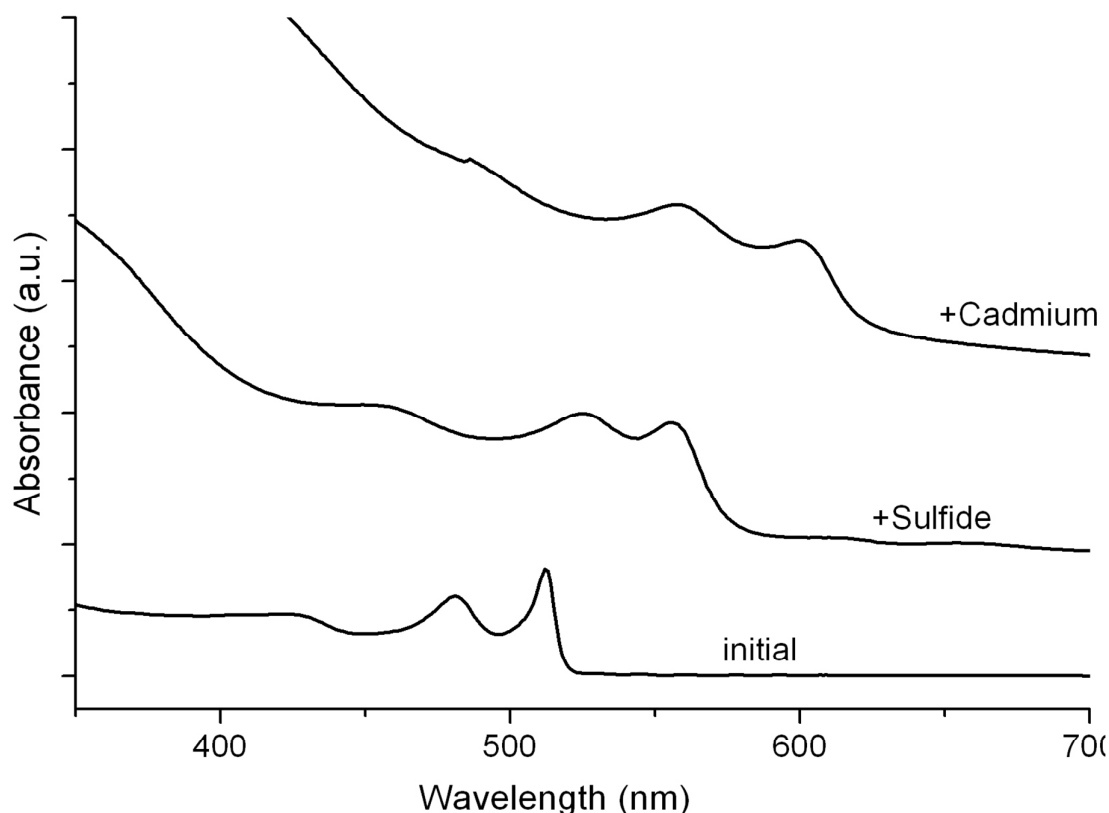


Figure S3: Absorbance spectra of the original CdSe platelets (down), after one S^{2-} monolayer deposition (middle) and after one S^{2-} and one Cd^{2+} monolayer deposition (up).

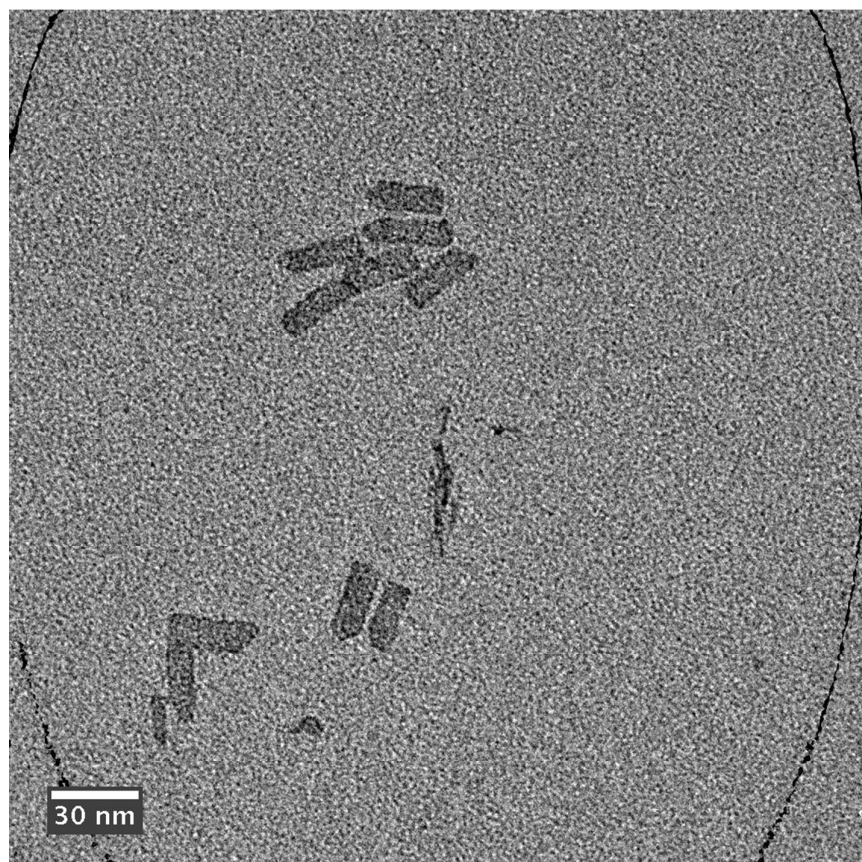


Figure S4: TEM picture of the final CdSe/CdS core/shell nanoplatelets.

H₂S as the sulfide source

Synthesis protocol:

400 μ L of the as-synthesized nanoplatelets in hexane diluted in 2 mL Chloroform were put under magnetic stirring into a glove-box. 2 mmoles H₂S are bubbling into the solution, the color change from yellow to orange and aggregation occurs. The aggregated platelets are precipitated by centrifugation and dispersed in hexane. 10 mg of Cd(Acetate)₂(H₂O)₂ are added and induce an other color change. After one hour, 200 μ L oleic acid is added into the solution, which becomes clear, indicating the dispersion of the platelets. The final CdSe/CdS core/shell platelets are precipitated with ethanol and suspended in hexane

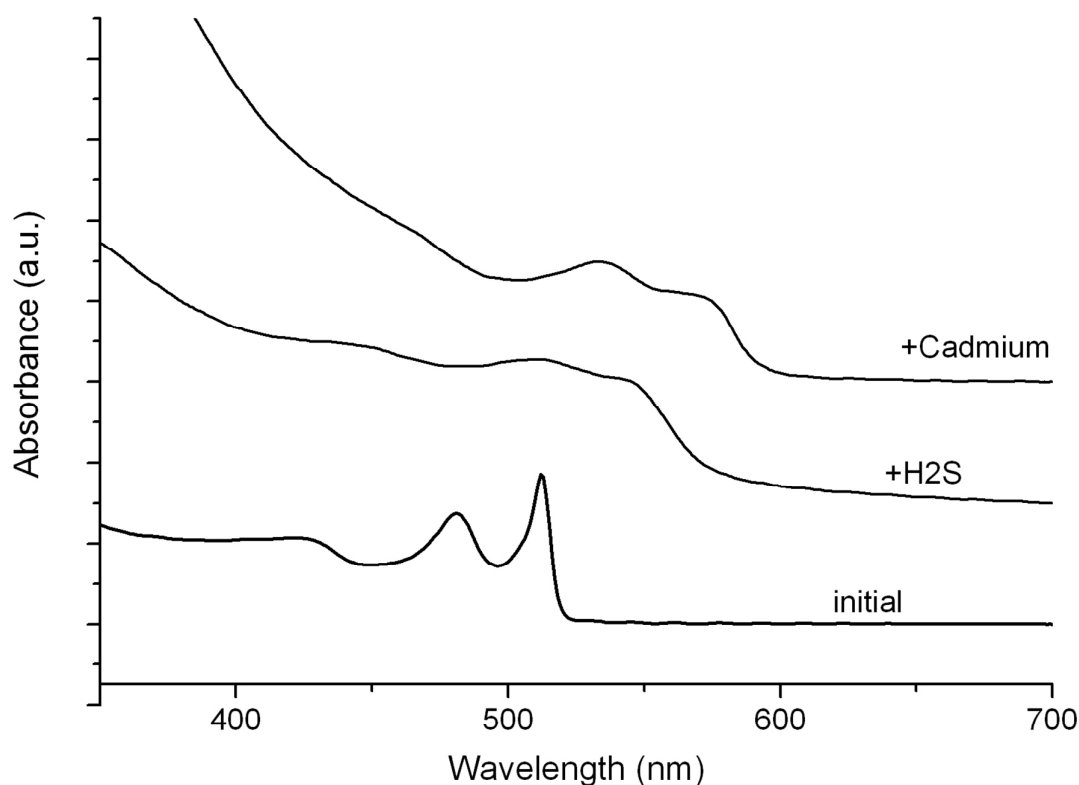


Figure S5: Absorbance spectra of the original CdSe platelets (down), after one S²⁻ monolayer deposition (middle) and after one S²⁻ and one Cd²⁺ monolayer deposition (up).

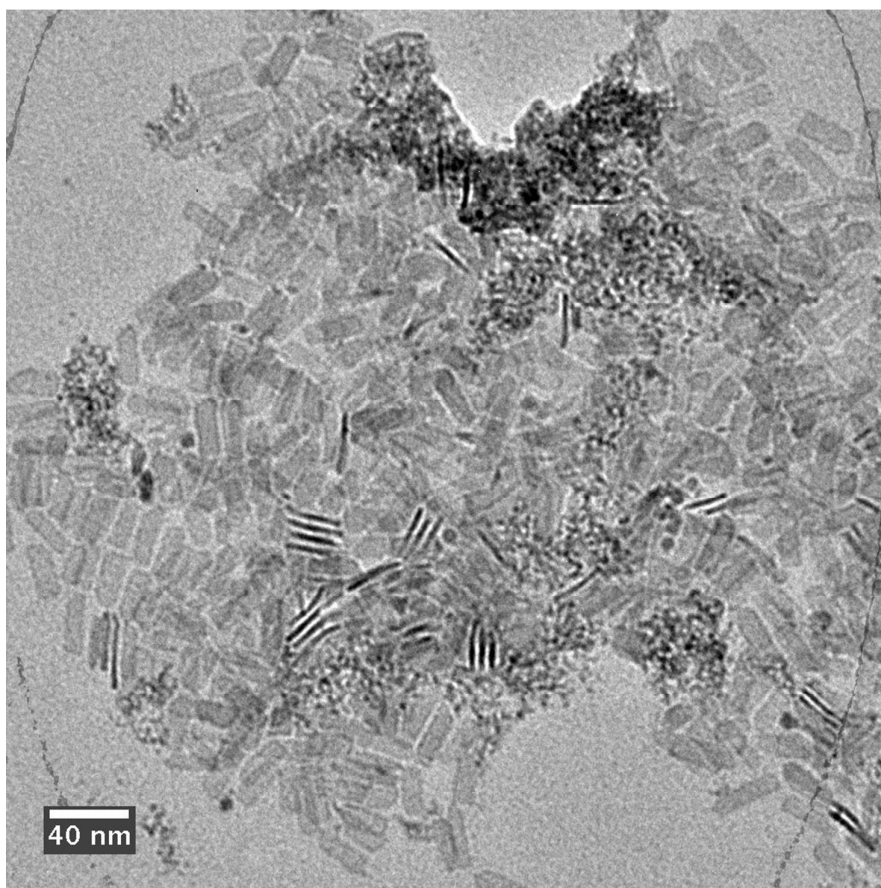


Figure S6: TEM picture of the final CdSe/CdS core/shell nanoplatelets.

EDX on core/shell CdSe/CdZnS NPLs

	sample1	Atomic %	sample2	Atomic %	sample3	Atomic %
Cd	15.71	34.97	12.12	33.58	11.28	32.95
S	20.35	45.30	17.03	47.19	16.81	49.11
Zn	5.48	12.20	4.2	11.64	3.7	10.81
Se	3.38	7.52	2.74	7.59	2.44	7.13
	44.92	100	36.09	100	34.23	100
S+Se		52.83		54.78		56.24
Cd+Zn		47.17		45.22		43.76
		100				
Zn/(Zn+Cd)		25.86		25.74		24.70
Se/(S+Se)		14.24		13.86		12.67

Table S1: Values obtained by EDX quantitative analysis on a CdSe/CdZnS sample. The samples differ only by the area analyzed.

The values obtained are coherent with the theoretical values of a CdSe/Cd_{0.7}Zn_{0.3}S NPL of initial size 1.5 nm x 10 nm x 40 nm with an homogeneous 2.75 nm Cd_{0.7}Zn_{0.3}S shell:

% Zn/(Cd+Zn)	25.6 %
% Se/(S+Se)	14.6 %

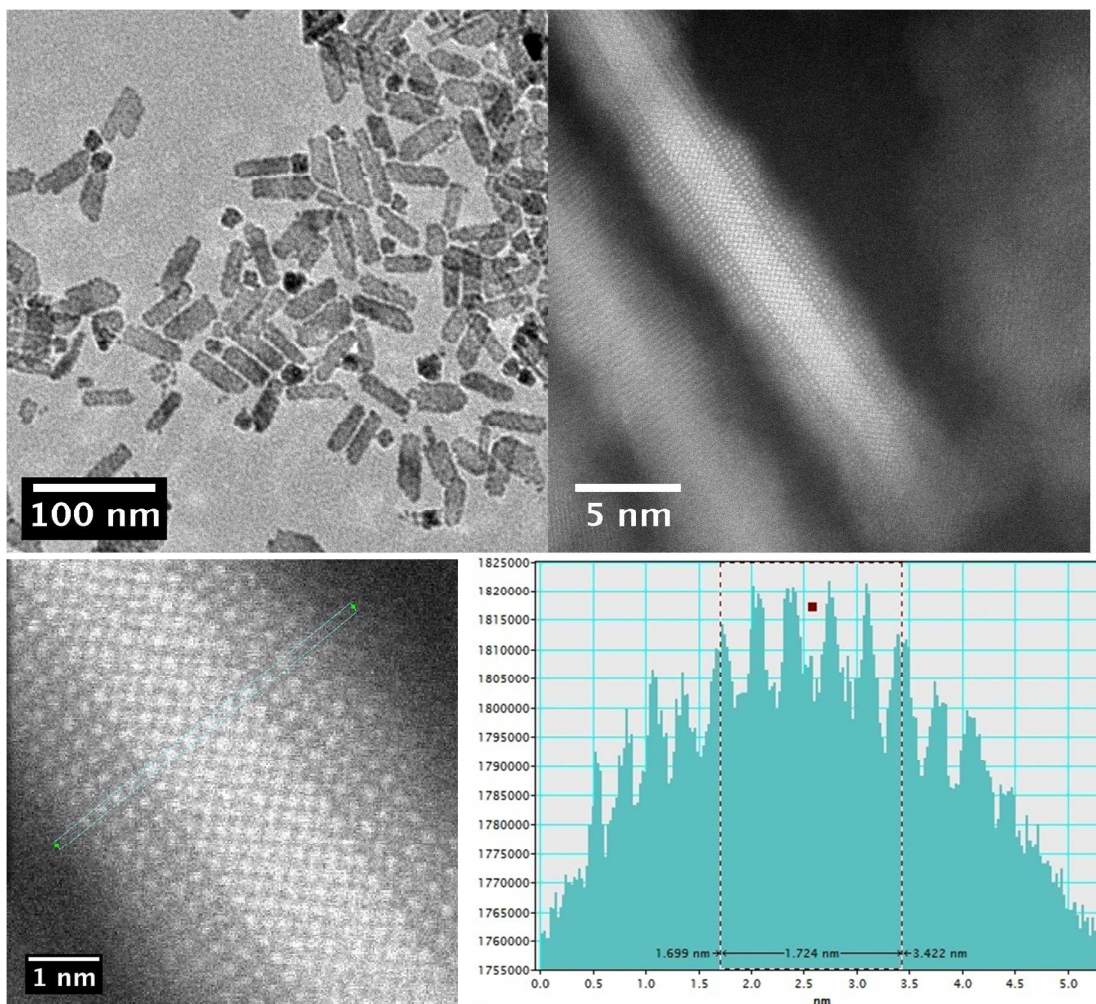


Figure S7: TEM picture of core/shell CdSe/CdZnS nanoplatelets whose core initially emits at 553 nm. Right: STEM-HAADF picture of a core/shell NPL standing on the edge revealing exactly 6 cadmium planes.

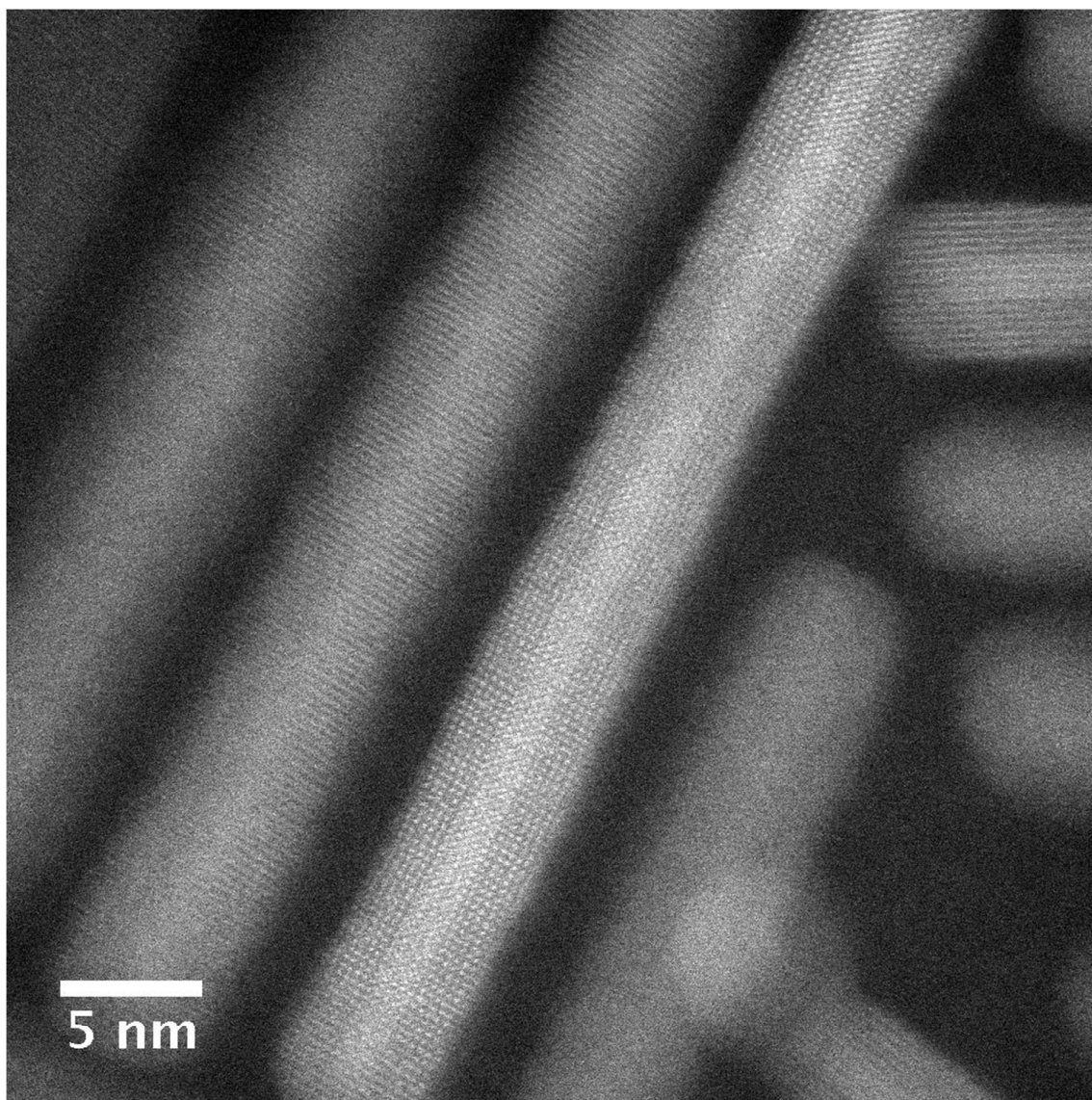


Figure S8: High Resolution HAADF picture of a CdSe/CdZnS core/shell nanoplatelet standing on the edge after annealing.

GPA (geometrical phase analysis) on CdSe/CdZnS core/shell nanoplatelets

We have used the Geometrical Phase Analysis (GPA) method to spatially map in detail the strain fields inside the core/shell nanoplatelets. The GPA method has been applied from atomic resolution HAADF-STEM image. Phase images have been calculated from two (200) peaks of the FFT. The x axis is aligned with the $\langle 001 \rangle$ direction of the nanocrystal. The spatial resolution of the strain map, fixed by the mask diameter selected for the phase image calculation, is given at about 1.2 nm.

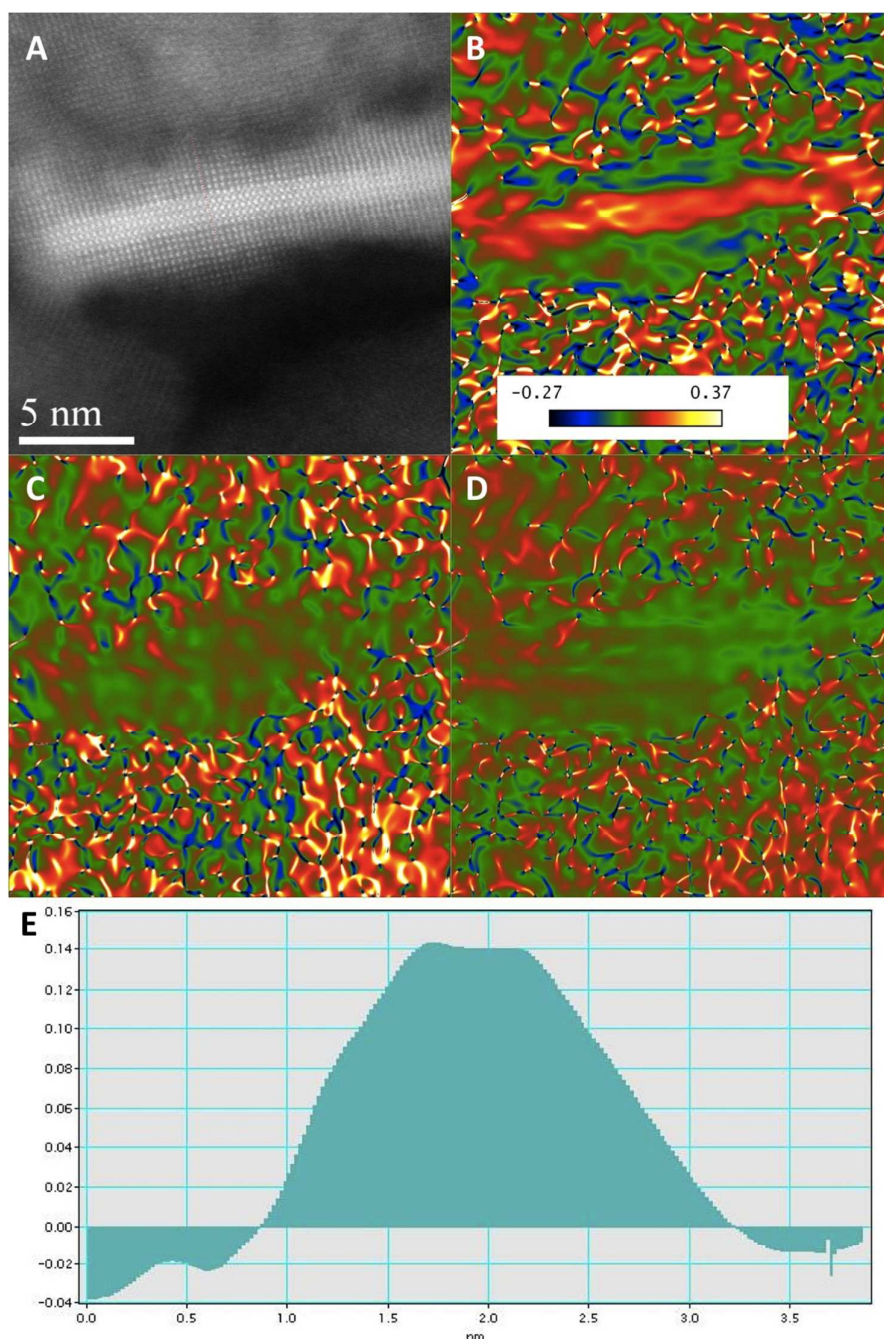


Figure S9: (A) High Resolution STEM-HAADF picture of a CdSe/CdZnS core/shell nanoplatelet standing on the edge. (B), (C): Deformation maps obtained by GPA, respectively E_{xx} and E_{yy} . (D): Rotation map R_{xy} . (E): Line profile of the deformation E_{xx} .

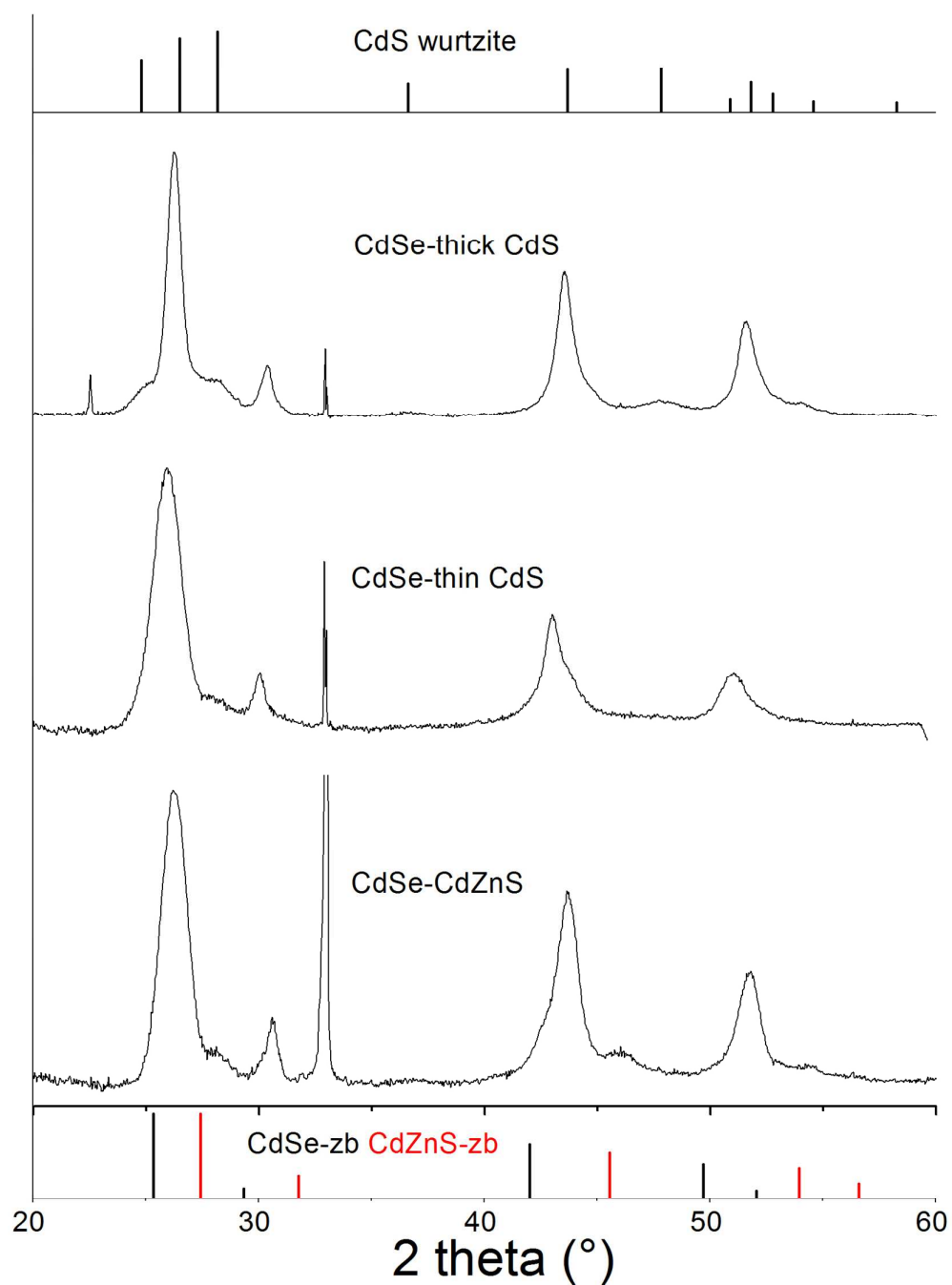


Figure S10: X-ray powder diffractograms of different core/shell nanoplatelets.

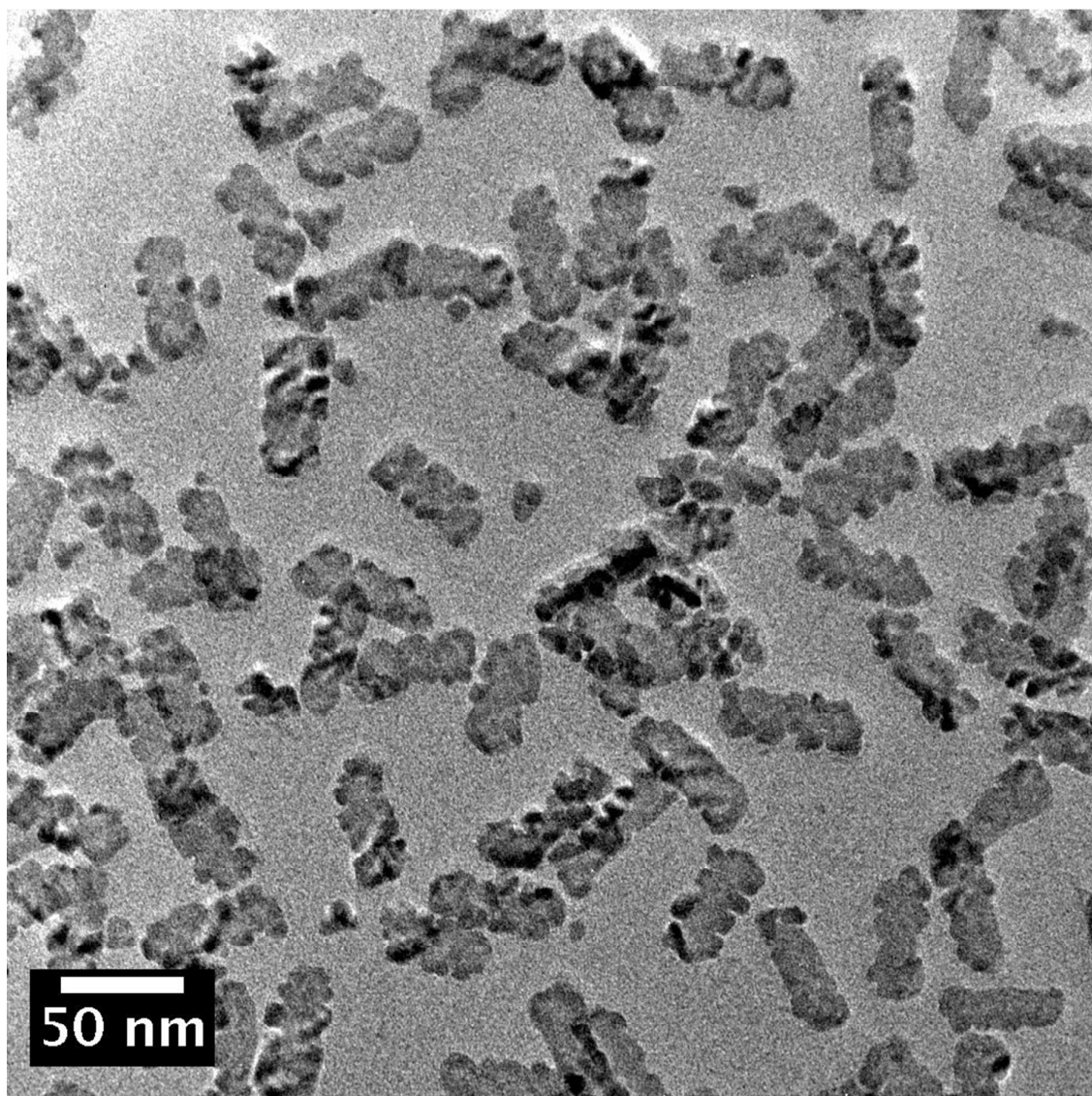


Figure S11: TEM picture of the core/shell CdSe/CdS sample with a thicker CdS shell showing some polytypism.

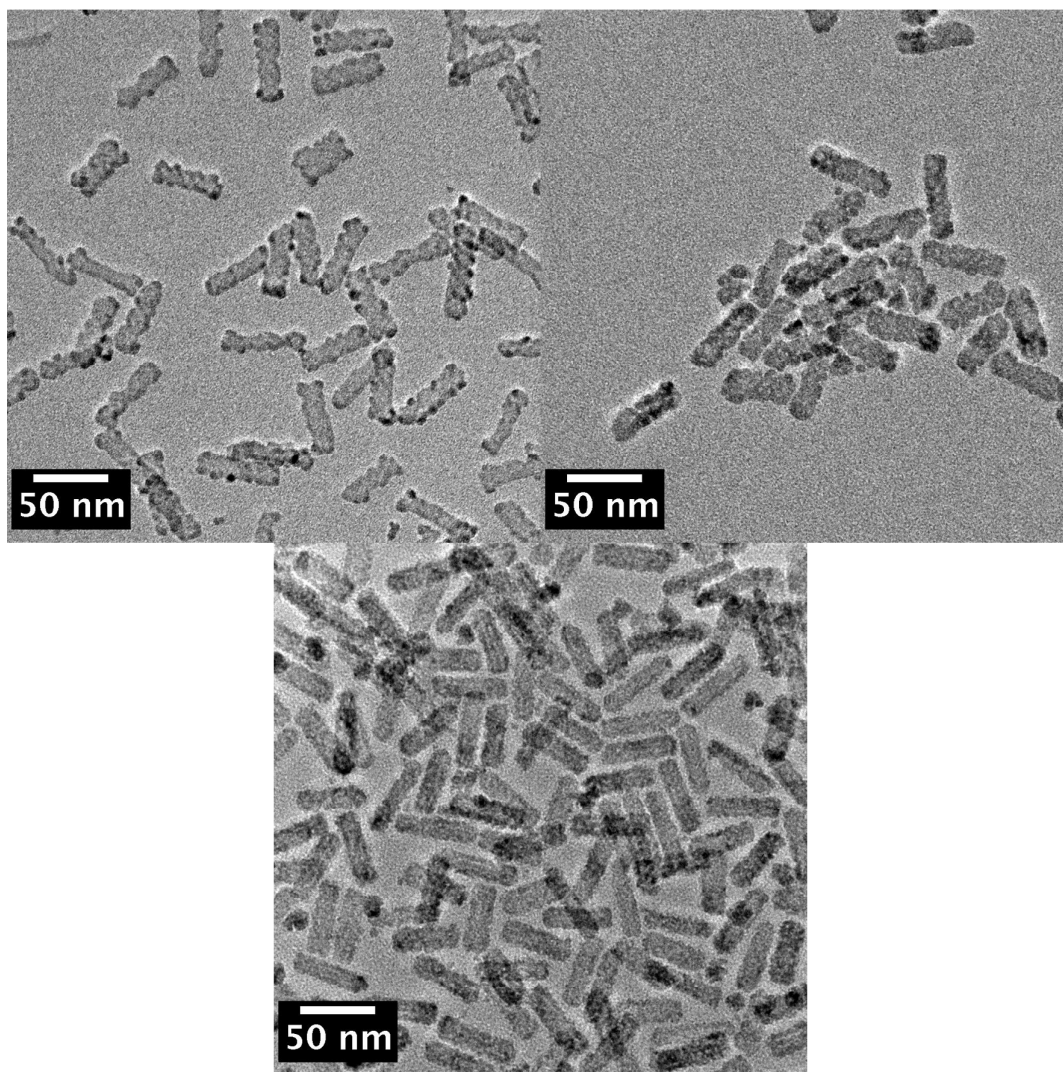


Figure S12: TEM pictures of three different shells on CdSe nanoplatelets. The shell is composed in CdS only (top left), Cd_{0.9}Zn_{0.1}S (top right) or Cd_{0.7}Zn_{0.3}S (bottom).

Large CdSe nanoplatelets synthesis

- Preparation of the injection solution:

0.36 mmol of $\text{Cd}(\text{Ac})_2$ are dissolved into 1 mL ethanol by mild heating. 0.12 mmol of oleic acid and 4.3 mL of SeODE are then added to the solution. 1 mL of butanol is added in order to have a monophasic, stable solution.

- Synthesis and growth of extended 5 monolayers' platelets:

15 mL of ODE are degassed for 15 minutes under vacuum in a three-neck flask. Under Argon, at 240 °C, the precursors' solution is injected at a rate of 5 mL/h. At the end of the injection, 2 mL of oleic acid are added in the flask, which is then cooled down rapidly. The solution is diluted in hexane and centrifugated at 5000 rpm. The precipitate is suspended in 10 mL hexane.