Supporting information for:

Crystal Phase Transitions in the Shell of PbS/CdS Core/Shell Nanocrystals influences Photoluminescence Intensity

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Characterization Techniques

Transmission Electron Microscopy

A JEOL 2011 FasTEM transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV was used to obtain high resolution TEM images. The direct electron beam intensity used for imaging mode was detected by a CCD camera. The TEM images were created and analyzed by a supplementary Digital Micrograph software package. TEM image contrast differences can be created by many types of amplitude and phase contrasts. S1

Figure S1: Bright field (a-c) and dark field (d,e) TEM images of large PbS/CdS core/shell NCs after 3 h exchange time. High resolution TEM images of a single PbS/CdS NCs are shown in (c-e). In (d) only RS electron diffraction peaks are used for the image creation, whereas in (e) only ZB peaks.

In this work, the darkfield images in Figure S1d,e were created by using diffraction contrast. In Figure S1d only the electron diffraction spots characteristic for the rocksalt (RS) crystal structure were used and in Figure S1e only zincblende (ZB) peaks were used for image formation. Thus the bright regions in S1d mainly concentrated in the core corresponds to regions depicting the RS crystal phase, whereas in S1e the bright parts within the shell
region originate from ZB crystal phases.

**Anomalous Small Angle X-ray Scattering**

Small angle x-ray scattering (SAXS) is a method widely used in the analysis of nanoscale structures.\(^{S2}\) The technique provides a number of structural parameters such as size and shape of particles, as well as their correlations and hence their volume fraction in the case of a denser particle system. In extension to SAXS, anomalous SAXS (ASAXS)\(^{S3-S6}\) allows element specific contrast variation between different phases in the sample and hence the possibility to determine chemical compositions as a function of particle dimension.\(^{S7,S8}\) The contrast variation in ASAXS is due to the dependency of the atomic scattering factor \(f(E)\) on the x-ray energy \(E\), in particular, in the vicinity of x-ray absorption edges. Hence, for ASAXS experiments synchrotron x-ray sources have to be used where the x-ray energy can be continuously varied. The ASAXS-spectra for the *large* and *small* sample series have been measured at the 7T-MPW-SAXS beamline at the BESSY II synchrotron (HZB Berlin, Germany), whereas the *medium* sized NCs have been recorded at the beamline ID01 at the European Synchrotron Radiation Facility ESRF (Grenoble, France).

For the case of the PbS/CdS core/shell nanocrystals the contribution of Pb as the strongest scatterer (with the atomic number \(Z = 82e^-\)) to the total scattering amplitude \(f(Z, E)\) can be varied by tuning the x-ray energy just below, e.g., the Pb-LIII-edge at \(E = 13.035\) keV. The atomic scattering factor \(f(Z, E)\) can be written as:

\[
f(E) = f_0 + f'(E) + if''(E)
\]  

where \(f_0 + f'(E)\) is the real part and \(f''(E)\) the imaginary part of the scattering amplitude. \(f_0(Z)\) depends only on the number of electrons in an atom, whereas \(f'(E)\) and \(f''(E)\) depend on the used x-ray energy. Thus the total amplitude \(f(E)\) deviates from the atomic number \(Z\) by varying the energy around an elemental absorption edge. The dispersion
corrections \( f'(E) \) and \( f''(E) \) are related to each other by the well known Kramers-Kronig relations and the values of the scattering factors were calculated by the procedure described by Cromer&Libermann.\(^{39}\) Hence, in ASAXS the scattered intensity is a function of the scattering vector \( \mathbf{q} \) and the x-ray energy \( E \), with \( q = 4\pi \sin \theta / \lambda \) and \( \lambda \) the x-ray wavelength:

\[
I(q, E) = F_0^2(q) + 2f'(E)F_0(q)F_R(q) + [f'(E)^2 + f''(E)^2]F_R^2(q) 
\]  

This equation consists of three parts: the energy independent normal SAXS term \( F_0^2(q) \), the scattering cross term containing the resonant and non-resonant part \( F_0(q)F_R(q) \) and the pure resonant term \( F_R^2(q) \), which is related to the Pb-electron density. By using equation 2, the over determined system of \( m \) equations for \( m > 3 \) measured energies can easily be solved numerically. The solution of this set gives the values of the three variables \( F_0(q) \), \( F_0(q)F_R(q) \) and \( F_R(q) \).\(^{37,38}\) The form factor \( F_{CS} \) for a spherical core/shell particle is derived by subtracting the analytical form factor of a homogenous inner sphere (the core) from the outer sphere.

\[
F(q, E)_{CS} = 3\Delta \eta_{shell}(E) \frac{\sin qr_{out} - (qr_{out}) \cos qr_{out}}{(qr_{out})^3} + 3(\Delta \eta_{core}(E) - \Delta \eta_{shell}(E)) \frac{\sin qr_{core} - (qr_{core}) \cos qr_{core}}{(qr_{core})^3},
\]

where \( r_{core} \) denotes the radius of the inner sphere and \( r_{out} \) is connected to the shell thickness \( t_{shell} \) by \( r_{out} = r_{core} + t_{shell} \). \( \Delta \eta_{core}(E) \) is the energy dependent scattering length contrast between the core and the solvent, and \( \Delta \eta_{shell}(E) \) between the shell and the solvent. \( \Delta \eta_{core,shell}(E) \) can be split using Eq. 1 into a non-resonant and a resonant, i.e., energy dependent part:

\[
\Delta \eta_{core,shell}(E) = \Delta \rho_{core,shell}r_e + \Delta \nu_{core,shell}(E)r_e,
\]
where $r_e$ is the classical electron radius and $\Delta \rho_{\text{core,shell}}$ the total electron density difference and $\Delta \nu_{\text{core,shell}}$ the Pb-electron density difference between the nanocrystal and the solvent. Hence, equation 2 was solved for each set of 5 scattering curves with a single spherical core/shell model using $r_{\text{core}}$, $t_{\text{shell}}$, $\Delta \nu_{\text{core,shell}}$, $\Delta \rho_{\text{core,shell}}$ as well as the total size distribution $\sigma$ as fit parameters. The size distribution width $\sigma$ is assumed to be the same for the core and the shell.

As an example, in Figure S2a 5 experimental scattering curves are shown together with the model fits for the medium core/shell NCs measured after 18 h exchange time. In Figure S2b one set for the small NCs after 29 h reaction time is depicted. All scattering curves have been calibrated into absolute units (i.e. macroscopic scattering cross-sections in units of cross-section per unit volume $cm^2/cm^3 = cm^{-1}$). For all energies the scattering of the solvents toluene and hexane was measured with the same statistical accuracy and was removed from the scattering curves of the sample before applying the fitting procedure. The accordance between data and fit is good, small deviations are only visible at larger $q$-values at low intensity values, where the error band of the scattering data is getting larger. By varying randomly the scattering data within the experimental error band and repeating the fitting procedures up to 20 times the stability of our results is tested and the errorbars for the density profiles (Figure 2, the main text) is obtained.
Figure S2: (a) Experimental ASAXS curves (symbols) fitted with a unique spherical core/shell model (lines) for the medium sized core/shell PbS/CdS NC-sample after 18h reaction time. The scattering cross section $I(q, E)$ plotted over the scattering vector $q$ were recorded at 5 different x-ray energies below the Pb-L$_{III}$-edge. The curves, except the black ones measured at an energy far from the edge, are each shifted vertically by a factor of 2 to lower values for clarity. (b) The same as in (b) for the small core/shell particles after 29h reaction time. Here, the factor for the shift is 4.
1-core/2-shells Profile for the Small NCs

The ASAXS procedure described above gives for the core/shell profile of the small NCs (see Figure 2d in the main text) an inconsistent result for the CdS shell: A significant amount of Pb is detected within the CdS shell, but the total electron density is strongly reduced with respect to the theoretical CdS bulk value (see Figure S3b). A nearly two times heavier element like Pb \((Z = 82)\) compared to Cd \((Z = 48)\) should result in contrary in an increased electron density. This problem can be solved, when we use for the fitting procedure a 1-core/2-shells model. The motivation for assuming a not homogenous Pb distribution within the shell is based on the proposed mechanism for shell formations due to cationic-exchange detailed described very recently for ZnSe/CdSe NCs.\(^\text{S10}\) The exchange starts with a fast Cd\(^{2+}\) for Pb\(^{2+}\) exchange on the outer most surface layer, followed by a slower thermally activated solid-state cation diffusion. For a shell thicker than 1 monolayer (ML) CdS the Cd-ions have to diffuse inwards, whereas the Pb-ions outwards. This can be realized by the formation of Frenkel-pairs:\(^\text{S10}\) The Pb\(^{2+}\) cations are diffusing towards the surface on interstitial lattice positions whereas Cd\(^{2+}\) is diffusing inwards over the Pb\(^{2+}\) vacancies. The surface Pb is finally removed from the surface by Cd-oleatic compound. This process is driven by the larger Cd-S bond strength with respect to PbS.\(^\text{S11}\)

If, however, the Cd-oleate concentration in the solution is too small a certain amount of Pb\(^{2+}\) will remain on the NC surface. From the ASAXS fits using the 1-shell model we receive \(4.5 \pm 0.25 \text{ Pb/nm}^3\) within the CdS shell of the small \((D = 4.7 \text{ nm})\) NCs after 29 h exchange time. This Pb amount would corresponds to a \(\sim 75\%\) surface coverage of one monolayer of Pb on top of the NCs. Thus in a 2-shell fit, a surface shell with different electron density should be detectable with a thickness in the range between two times the ionic radius of Pb with 0.133 nm\(^\text{S12}\) and the ML thickness of PbS along the [1 1 1] direction of around 0.34 nm.

In Figure S3a the experimental SAXS curve (black spheres) of the small core/shell NCs after 29 h exchange time is shown far from the Pb absorption edge at an x-ray energy of 12923 eV. The black solid line represents the the 1-shell ASAXS fit retrieved from minimizing
Figure S3: (a) Experimental ASAXS curve (symbols) measured at 12923 eV x-ray energy, together with the 1-shell ASAXS fit (black line), a 2-shell SAXS fit (blue line), a two shell simulation (cyan line), as well as a simulation assuming a large PbS core (red line) containing the whole detected Pb. (b) Resulting $e^-$-density profiles resulting from the 1-shell ASAXS fit (black) and the 2-shell SAXS fit (blue line). (c) Profiles for the simulated 2-shells profile assuming a sub-ML of PbS (cyan line) and the simulated large PbS core (red line).
the error between experimental data and fit for all 5 scattering curves simultaneously (see Figure S3a). The resulting electron density profile is shown in Figure S3b also as black line. For the 1-core/2-shells fit at this fixed energy we use the program DECON developed for retrieving the density profiles of polydisperse colloidal particles. The blue line in Figure S3a shows the resulting fit with the lowest mean deviation for a physical feasible electron density profile depicted in Figure S3b. Indeed, we receive a surface shell with reduced $e^-$-density of 800 $e^-$/nm$^3$ and of 0.38 nm thickness, but the $e^-$-density of the 1. intermediate CdS-shell with 960 $e^-$/nm$^3$ reaches nearly the theoretical bulk value of 1000 $e^-$/nm$^3$ (blue line in Figure S3b).

Moreover, we can estimate the expected electron density of a 0.38 nm surface layer consisting of a 1 ML of Pb with 75% coverage. This estimation results in about 890 $e^-$/nm$^3$, which is in good accordance to the retrieved fit result. Additionally, we simulated a scattering curve based on the retrieved 2-shell profile, but assume a PbS-surface shell with 75% coverage depicting with 1300 $e^-$/nm$^3$ a higher electron density with respect to the intermediate CdS shell (dashed cyan line in Figure S3c). This resulting SAXS curve (cyan line in Figure S3a) shows, however, a slightly larger mean deviation with respect to the experimental data as compared to the 2-shells fit with a pure Pb-surface (blue line). (The mean deviation is weighed with the width of the experimental error band and thus the deviations at smaller $q$-values are more significant than at larger $q$-values, where the error band is increased.)

Furthermore, one can assume a third alternative Pb distribution within the small PbS/CdS NCs, where all the Pb found in the shell is concentrated around the remaining PbS core (see sketch in Figure S3d). We calculate the core volume that can contain the total Pb-amount of about 250 Pb atoms within the whole NC. For this a core diameter of nearly 3 nm with the theoretical Pb-concentration for PbS of 18.9 atoms/nm$^3$ is needed as depicted as red line in the density profile of Figure S3c. The resulting simulated scattering curve (red line in Figure S3a) shows no agreement with the experimental data.

Finally, from this we can conclude that the detected shell-Pb for the small NCs is not ho-
mogenously distributed within the CdS-shell, but also not concentrated around the remaining PbS core. The remaining shell-Pb is most probably distributed on top of the CdS surface shell forming the outer most surface layer as sketched in Figure S3d. This Pb-distribution is found to be in good agreement with the proposed mechanism for a shell growth driven by cationic exchange.\textsuperscript{10}

Rutherford Backscattering Spectrometry

The Rutherford Backscattering Spectrometry (RBS) method is based on elastic collisions between energetically light ions (H, He with a few hundred keV up to 2 MeV) and the atomic nuclei in a stationary sample. Thus the method is free from any matrix effects. Scattering kinematics permits to identify the elements present in a thin layer from the yield of particles backscattered from the sample in a large angle. RBS measurements were performed, employing the Van de Graaff accelerator AN700 (30 - 700 keV).\textsuperscript{14} The low beam currents employed guarantee a non-destructive analysis of the samples. Scattered ions were detected by two semiconductor surface barrier detectors. The Monte Carlo program SIMNRA\textsuperscript{15} was used to evaluate the sample compositions by fitting the peaks corresponding to the individual elements in the measured spectra as shown in Fig. S4. Note, that the substrate signal does not influence the analysis.

**Sample preparation.** Toluene and TCE solutions of PbS, PbS/CdS, and PbS/CdS/SiO2 NCs were spin-coated at 2000 rpm for 3 min. The concentration was adjusted in a range of 5-10 mg/ml in order to obtain (sub-)monolayers of NCs. The HF-treated polished silicon was used as a substrate. In Table S1 the RBS results from the large and the small sample series are summarized together with the total Pb concentration derived from the ASAXS density profiles. For the medium sized NC sample series no RBS-data are available.
Figure S4: (a) RBS spectrum of a one monolayer thick NC film consisting of large PbS/CdS NCs after 1 h reaction time, presented along with the results of Monte Carlo simulations. Silicon is used as substrate.

Table S1: Composition of PbS NCs and PbS/CdS NCs after different times of Cd\(^{2+}\) treatment (the contents are given in atomic %)

| samples         | time | Pb     | Cd     | S      | ASAXS (at.%) Pb |
|-----------------|------|--------|--------|--------|-----------------|
| PbS             | 0 h  | 49±0.7 | 0      | 51±1   | 44.3±2.3        |
| PbS/CdS         | 1 h  | 30.8±0.6 | 20.0±1.1 | 49.2±1.7 | 33.3±2.3        |
| PbS/CdS         | 2 h  | 28.9±0.7 | 21.5±1.3 | 49.5±2  | 32.8±1.2        |
| PbS/CdS         | 3 h  | 26.7±0.7 | 26.3±1.2 | 47.0±1.9 | 26.47±0.6       |
| small NCs       |      |        |        |        |                 |
| PbS             | 0 h  | 53.0±2.2 | 0      | 47.0±2.2 | 49.5±4          |
| PbS/CdS         | 1 h  | 16.7±0.8 | 35.8±1.4 | 47.4±2.2 | 19.2±1.4        |
| PbS/CdS         | 6 h  | 12.9±0.6 | 39.5±1.2 | 47.7±1.8 | 13.3±1.1        |
| PbS/CdS         | 29 h | 12.5±0.8 | 39.8±1.6 | 47.7±2.4 | 18.6±1.8        |
Photoluminescence spectroscopy data and peak shift analysis

All samples were measured under identical conditions, allowing to compare PL intensities of different samples. To quantify the luminescence enhancement the optical density of all samples was adjusted to have the same value at a wavelength of 500 nm. Thus the relative change in the PL intensity is proportional to a relative change in the quantum yield. The integral PL emission values of all three samples series were derived from the total area under the PL emission spectra. The large NCs depicts peak wavelengths between 1700 nm and 1900 nm (see Figure 1(c) in the main text), the medium sized NCs between 1500 nm and 1600 nm and the small NCs between 1150 nm and 1350 nm as shown in Figure S5(a) and (b). The faint shoulders on the left side of the two core/shell peaks in Figure S5(a) are produced by the water absorption line at around 1400 nm wavelength and are not related to the PbS/CdS PL signal. (The measurements have been performed in air.) These parts of the curves have been excluded from the integrated area.

\[ E_0 = \frac{hc}{\lambda_{max}} \]

Figure S5: (a) PL spectra of medium sized PbS and PbS/CdS NCs with diameters \( D \) of around 6 nm, measured after different reaction time steps. (b) The same for the small PbS and PbS/CdS NCs with 5 nm diameter.

Additionally, we analyze additional to the total integrated PL peak intensity, the peak wavelength \( \lambda_{max} \) as a function NC diameter, shell thickness and crystalline phase fraction within the shell. The peak wavelength is related over \( E_0 = \frac{hc}{\lambda_{max}} \) to the band gap energy.
$E_0$ of the quantum dot, with $h$ as the Planck constant and $c$ the speed of light. PbS is a narrow gap semiconductor, with a bulk band gap of 0.41 eV, and a large exciton Bohr radius of around 18 nm.\textsuperscript{S16} The PbS band gap $E_0$ can be tuned by varying the particle diameter over a large spectral range in the near infrared. When the NC diameter is decreased $\lambda_{\text{max}}$ depicts a blue shift, thus $E_0$ value is shifted to higher energy values. This sizing curve of the band gap energy $E_0$ derived empirical from Moreels et al.\textsuperscript{S16} follows a modified $1/d$ law, with $d$ the PbS NC diameter:

$$E_0 = 0.41 + \frac{1}{0.025d^2 + 0.283d}$$

Additionally to this size effect the PL energy can be shifted to longer wavelengths due to an transfer of excitonic energy to the molecular vibrational modes of organic ligands on the NC surface.\textsuperscript{S17} An even stronger effect due to the large excitonic Bohr PbS is expected for PbS NCs covered with a shell, where the excitonic wave function can extend into the shell region, depending on the band gap of the shell material relative to the core material (for a review see Ref. \textsuperscript{S18}). A strong effect on the PL is expected for an energy level alignment between core and shell, where either the hole or the electron wave function is localized within the shell. For this staggered type-II band alignment\textsuperscript{S18} a significant red-shift of the emission peak wavelength is expected, when the core is covered by a shell. In the PbS/CdS core/shell systems, a small conduction-band offset and a large valence-band offset suggest that the electron wave functions extend into the CdS shell, while holes are efficiently confined in the PbS core.\textsuperscript{S19}

For the case of our investigated large, medium and small sized core/shell NCs we expect, a blue-shift due to the shrinking core and an additional a red-shift with increasing shell thickness. Furthermore, if the $RS - ZB$ phase fraction within the CdS shell as a significant influence on the band structure alignment, we should observe an additional shift of the emission peak energy.

For this analysis we have plotted the experimental PL peak energy derived from $\lambda_{\text{max}}$ of
Figure S6: (a) PL peak energy as a function of the diameter of the large, medium and small NCs shown as black, cyan and green squares. The full squares represents the pure PbS NCs without shell, whereas the open symbols the PbS/CdS core/shell NCs. The red line is the empirical relation between band gap energy and NC diameter found by Moreels et al.\textsuperscript{516} for PbS NCs. (b) The same data as in (a) but corrected with the core diameter. (c) The PL peak energy corrected with the core diameter and normalized to the shell thickness as a function of the $RS \rightarrow ZB$ phase fraction within the shell.
all NC samples as a function of the NC core-diameter together with the sizing curve of the band gap energy $E_0$ of equation 5 in Figure S6. It can be clearly seen that all pure PbS NCs without CdS shell and the large NCs with the thin shell below 1 nm nicely follows this sizing curve, i.e. the PL peak energy is shifted to higher energies with decreasing PbS core. The PL energy of the medium and small core/shell NCs with thick shells above 1 nm depicts, however, a significant deviation from this curve (see Figure S6a). That means apart from the blue-shift of the PL peak due to the shrinking PbS core, $\lambda_{\text{max}}$ is additionally red-shifted, i.e. shifted to lower energy values. To study this shell induced effect in more detail, we normalized the PL peak energy values to the NC diameter using equation 5 as shown in Figure S6b. This core corrected PL energies for the pure PbS NCs and for the thin shell core/shell NCs are now rather constant over the NCs diameter as expected. The PL peak energies for the medium and small core/shell samples shows in contrast a strongly decreased energy value as a function of the shell thickness. The lowest PL energy is found for the largest shells of around 2 nm thickness. This is in agreement with the model proposed for the type-II staggered band gap alignment, where the electron wave function of the exciton extends into the shell. With increasing CdS shell and larger separation of the electron-hole pair, the effective band gap is decreased and results in a red-shift of the emission peak.\textsuperscript{518}

Furthermore, we can check, if the amount of the metastable $RS$ crystal phase within the shell has any influence on the the band gap alignment and thus on the PL emission. In Figure S6c the double normalized PL energy values are shown, i.e., normalized to the NC diameter as well as to the shell thickness. These relative PL values are plotted over the $RS - ZB$ phase fraction within the shell, where the amount of the $RS$ phase varies within the shell from about 90% down to 5%, when the CdS shell reaches its equilibrium $ZB$ crystal structure. In Figure S6c there is no influence of the crystal structure on the PL peak energy observable, and hence on the band alignment.

To conclude the analysis of the PL peak wavelength values, we can sum up three experimental findings.
i.) The emission peak wavelength values of the pure NCs and the core/shell NCs with thin shells follow very well the sizing curve found for the band gap energy $E_0$ of PbS NCs. The $\lambda_{\text{max}}$ value is shifted to shorter wavelengths with decreasing diameter. This is an independent optical confirmation of the determined PbS core diameters derived by our ASAXS method.

ii.) This size induced blue-shift is partly compensated for the medium and small sized core/shell NCs due to a shell induced red-shift. This red-shift increases with increasing shell thickness and can be related to an extension of the excitonic wave function into the CdS shell.

iii.) The crystalline phase within the shell, either $RS$ or $ZB$, has no influence on the PL wavelength and hence no significant impact on the core/shell band alignment.
Analysis of the experimental derived x-ray diffraction data

In the Figures S8(a), S9(a), S10(a) all experimental derived x-ray diffraction (XRD) patterns of all investigated sample series together with their fits (Gaussian peaks with background) are shown. To analyze the measured XRD data quantitatively we calculated the diffraction patterns for the pure PbS NCs and the PbS/CdS core/shell NCs by means of the Debeye-formula,

\[ I(q) = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i(q)f_j(q) \frac{\sin qr_{ij}}{qr_{ij}}, \]  

where we sum up over all atoms with the scattering factors \( f_i \) and \( f_j \) with distances \( r_{i,j} \) from each other by assuming the orientation of \( \mathbf{r} \) to vary randomly. The orientational average of the phase factor is \( \frac{\sin qr_{ij}}{qr_{ij}} \), with \( q \) as the scattering vector. We derive the atomic positions for Pb, Cd and S from their positions in their unit cell. We calculate the diffraction patterns for the 12 measured individual NC-ensembles with different core/shell dimensions. For this we fill up the core/shell volumes of the NCs as derived from ASAXS with the particular unit cells of PbS and CdS. We compute only two limiting cases for the diffraction pattern: The chemically uniform CdS shells are set either to depict fully the rock salt (Fm3m) crystal structure with the PbS lattice constant of 5.936 Å or the zinc blende structure (F43m) with the bulk CdS lattice constant of 5.518 Å. The crystal structure of the pure PbS NCs and the PbS-cores are kept constant in the RS phase (see sketch in Figure S7). At the core/shell border and the outer NC-surface the unit cells were cut atomically sharp. (For the case of the small core/shell NCs the incomplete surface Pb-monolayer was neglected in the calculation due to its small contribution to the total scattering signal.) For this purpose we have written an own simulation software PCG – SWAXS were the geometrical 1-core/1-shell parameters, the chemical composition as well the crystal structure can be varied freely.

The values of the integral peak intensities and the shift of the peak positions derived from the simulated patterns, give the maximum impact of the shell being either fully in the RS
Figure S7: Scheme to illustrate the crystal structures used in the calculations for the diffraction patterns: The pure PbS NCs as well as the PbS-cores are always kept in the bulk RS crystal structure of PbS. The CdS-shells are either fully in the RS structure of the core or fully in the equilibrium ZB crystal structure of CdS.

or ZB crystal structure (see Figures S8(b), S9(b), S10(b)). Comparing these values with the all experimental obtained values for the large, medium and small NCs allowed to determine quantitatively the RS – ZB crystal phase fraction within the CdS-shell.

For the large core/shell sample series the contribution of the thin shell to the total diffraction signal is only around 30% and hence the observed change in the peak ratio as well in the peak shift (see Figure S8) is lower, as compared to the thick shells of the medium and small sized NCs (see Figures S9 and S10). For these core/shell samples the contribution of the core is below 6% and thus the experimentally observed peak changes could be even directly related to the amount of RS-ZB phase fraction within the CdS shell (see Figures S9 and S10).
Figure S8: (a) The experimental diffraction pattern of the large NCs are shown (open circles) together with their fits (lines) for different exchange time steps. The vertical dashed lines mark the positions of the Bragg peaks for rock salt (RS) PbS and zinc blende (ZB) CdS bulk structures. The blue and red full squares mark the theoretical intensity values for bulk PbS and CdS. (b) The simulated diffraction pattern of the large NCs are shown (open circles) together with their fits (lines). The same fitting routine is used for the experimental and simulated data. The pattern for the pure PbS NCs is shown in black, whereas in cyan for a core/shell NC with a CdS-shell of 0.7 nm thickness and fully in the RS crystal structure; in red the same shell fully in the ZB structure. In blue the simulation for a 1:1 RS/ZB ratio within the shell is shown assuming an homogeneous distribution of the phases.
Figure S9: (a) The experimental diffraction pattern of the medium sized NCs are shown (open circles) together with their fits (lines) for different exchange time steps. The vertical dashed lines mark the positions of the Bragg peaks for rock salt (RS) PbS and zinc blende (ZB) CdS bulk structures. The blue and red full squares mark the theoretical intensity values for bulk PbS and CdS. (b) The simulated diffraction pattern of the large NCs are shown (open circles) together with their fits (lines). The pattern for the pure PbS NCs is shown in black, whereas in cyan for a core/shell NC with a CdS-shell of 1.4 nm thickness and fully in the RS crystal structure and in red the same shell fully in the ZB structure. In blue the simulation for a 1:1 RS/ZB ratio within the shell is shown assuming an homogeneous distribution of the phases.
Figure S10: (a) The experimental diffraction pattern of the small NCs are shown (open circles) together with their fits (lines) for different exchange time steps. The vertical dashed lines mark the positions of the Bragg peaks for rock salt (RS) PbS and zinc blende (ZB) CdS bulk structures. The blue and red full squares mark the theoretical intensity values for bulk PbS and CdS. (b) The simulated diffraction pattern of the large NCs are shown (open circles) together with their fits (lines). The pattern for the pure PbS NCs is shown in black, whereas in cyan for a core/shell NC with a CdS-shell of 1.9 nm thickness and fully in the RS crystal structure and in red the same shell fully in the ZB structure. In blue the simulation for a 1:1 RS/ZB ratio within the shell is shown assuming an homogeneous distribution of the phases.
Figure S11: The RS-ZB phase fraction as a function of the strain state within the CdS-shell is plotted for all three sample series. The values for the large, medium and small core/shell NCs with different shell thicknesses (black, cyan and green squares) are derived from the (220) peak positions. The straight lines are linear fits to the data. The maximum tensile strain of 0.02 for the CdS-shell (ZB, $a_{\text{CdS}} = 5.818$ Å) can be reached when the shell fully keeps the lattice constant of the PbS core (RS, $a_{\text{PbS}} = 5.936$ Å) marked with the red dashed line. The blue dashed line marks the value for the shell depicting the bulk lattice constant of ZB CdS. The negative compressive strain values for the 2 nm thick CdS-shells of the small sample series is related to an additional hydrostatic surface stress due to the small particle size.

Notes and References

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