

## Supporting information

# The Effect of Atomic Disorder at the Core–Shell Interface on Stacking Fault Formation in Hybrid Nanoparticles

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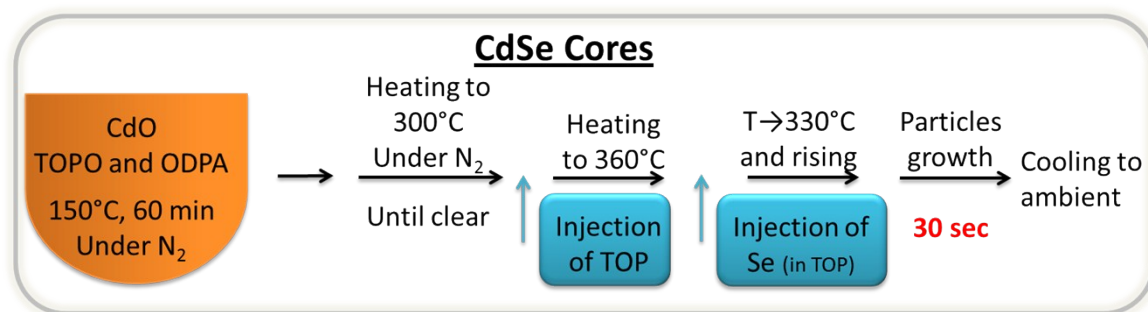
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### Materials

All the experiments in the paper were conducted using these materials : CdO (99.999%, Strem Chemicals, MA, USA), Se (99.999%, Alfa-Aesar, MA, USA), trioctylphosphine (TOP; 97%, Sigma-Aldrich, Israel), trioctylphosphine oxide (TOPO; 99%, Sigma-Aldrich, Israel), octadecylphosphonic acid (ODPA; 99%, Polycarbon Industries, MA, USA), S (99.98%, Sigma-Aldrich, Israel), oleic acid (90%, Alfa-Aesar, MA, USA), 1-Octadecene (ODE; 90%, Sigma-Aldrich, Israel), Octadecylamine (ODA ; 90%, Sigma-Aldrich, Israel), hexane (90%, Bio-Lab, Israel), toluene (90%, Bio-Lab, Israel).

### Synthesis of CdSe QDs:

We synthesized the CdSe cores according to the procedure shown by Amirav et al. {1}. CdO (0.06 g, 0.47 mmol), TOPO (3 g) and ODPA (0.313 g) were loaded into a 25 ml triple-necked flask and heated to 150°C. The system kept under N<sub>2</sub> flow for around 60 min in order to eliminate water residues and impurities in the solution, and then heated under N<sub>2</sub> flow to 300°C. Once the solution seems colorless, 1.8 ml of TOP were injected into the mixture, and the temperature was set to 360°C. Followed by a swift injection of a solution of 0.058 g Se (0.735 mmol) dissolved in 1 ml of TOP into the flask. After the injection the temperature decreased to 330°C, and the heating mantle was removed after 30 s of the growth phase (**Figure S1**). The obtained particles were precipitated by methanol, and isolated by centrifugation. Then, the precipitated nanocrystals were repeatedly washed by re-dissolution in toluene and precipitation in methanol. After the purifying procedure the nanocrystals were dissolved in toluene.



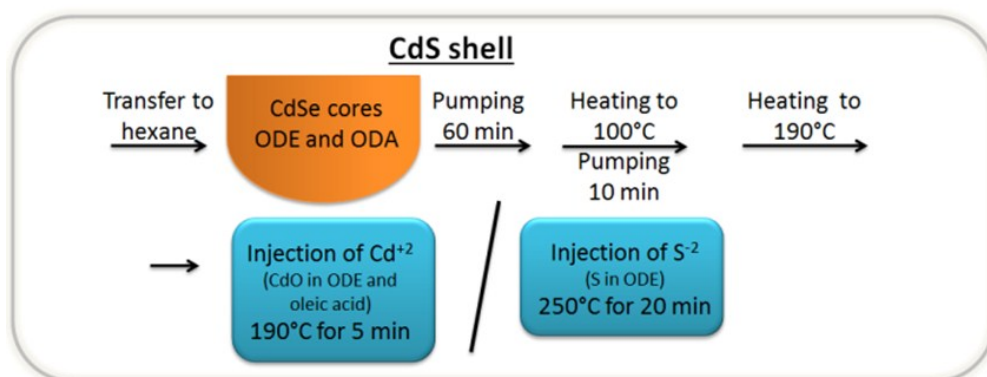
**Figure S1.** Schematic illustration of the CdSe cores synthesis procedure

### Synthesis of CdS shells:

The CdS layers were added according to a modification of the procedure described by Blackman et al. {2}. The pre-prepared CdSe cores were transferred to hexane ( $4.00 \cdot 10^{-5}$  mmol CdSe particles in 1.47 ml or 41.5 mmol hexane), the solution was then mixed with a mixture of ODA (0.604 g, 2.24 mmol) and ODE (2.55 ml, 8.00 mmol) in a 25 ml triple-necked flask. The system was pumped down at room temperature for 60 min in order to eliminate water residues and impurities, and then again for 10 min at 100°C. Next, the system was heated to 190°C followed by alternating injections of Cd<sup>2+</sup> and S<sup>2-</sup> solutions. The injection volume was calculated each time in order to contain the number of atoms required to produce a single monolayer. Therefore, each subsequent injection had larger volume, in order to completely cover the increasing interface of the particle.

The preparation of the Cd<sup>2+</sup> solution was as follows: CdO (0.040 g, 0.312 mmol) was dissolved in a mixture of oleic acid (0.786 ml, 2.49 mmol) and ODE (7.04 ml, 22.1 mmol) at 250°C in a 25-ml triple-necked flask. Obtaining a solution with a final concentration of 0.04 M of Cd<sup>2+</sup> ions. At the end of the process, the solution temperature was decreased to 60°C. The preparation of the S<sup>2-</sup> solution was as follows: elemental S (0.080 g, 0.312 mmol) was dissolved in ODE (7.80 ml, 24.50 mmol) at 200°C in a 25-ml triple-necked flask. Obtaining a solution with a final concentration of 0.04 M of S<sup>2-</sup> ions. At the end of the process, the solution was allowed to cool to ambient temperature.

The deposition of a CdS layer was as follow: first, the Cd<sup>2+</sup> solution was injected into the cores solution, and the temperature was maintained at 190°C for 5 min under N<sub>2</sub> flow. Then, the S<sup>2-</sup> solution was injected, the temperature was set to 250°C, and the solution was stirred for 20 min. Before each deposition cycle, the temperature was decreased to 190°C, and the procedure was repeated. The cycles were repeated until the desired number of layers in the shell was produced (**Figure S2**). At the end of the process, the solution was allowed to cool to ambient temperature; the obtained particles were transferred to a 125-ml separatory funnel, diluted with hexane, and extracted with the addition of methanol. The top hexane layer, which contained the particles, was transferred to a 15-ml centrifuge tube. The obtained particles were precipitated by acetone, and isolated by centrifugation. The precipitate was dissolved in toluene, and underwent the same cleaning procedure as detailed for the cores. The final product was dissolved in toluene.

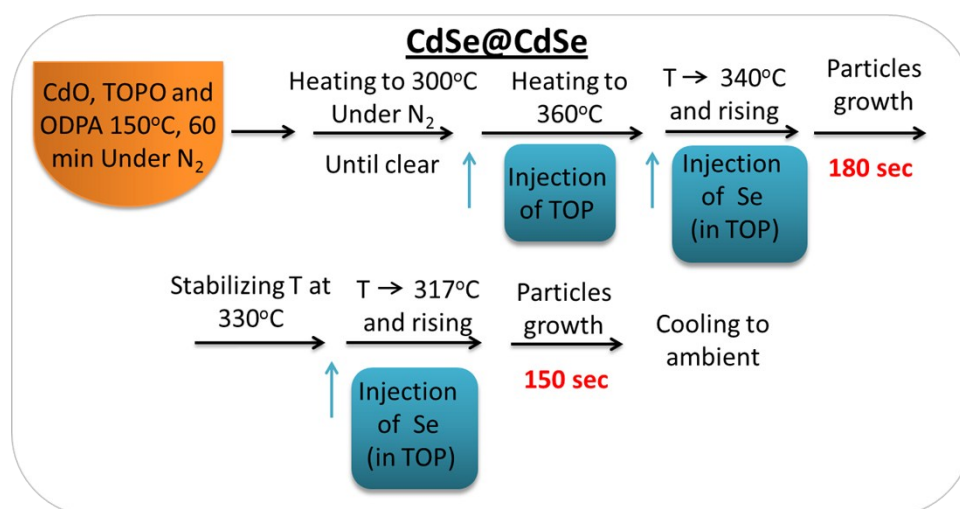


**Figure S2.** Schematic illustration of the CdS shell deposition procedure

### Synthesis the CdSe@CdSe particles

The CdSe@CdSe nanocrystals were synthesized according to the same procedure as the CdSe cores, but with some modifications: CdO (0.06 g, 0.47 mmol), TOPO (3 g) and ODPA (0.313 g) were loaded into a 25 ml triple-necked flask and heated to 150°C. The system kept under N<sub>2</sub> flow for around 60 min in order to eliminate water residues and impurities in the solution, and then heated under N<sub>2</sub> flow to 300°C. Once the solution seems colorless, 1.8 ml of TOP were injected into the mixture, and the temperature was set to 360°C. Thereafter, a solution of 0.058 g Se (0.735 mmol) dissolved in 1 ml of TOP was injected to the flask in two portions. First, 0.6 ml of the solution was injected to the flask. Followed, by a rapidly decrease of the temperature to 340°C, and a growth phase of 180 s. The temperature was then set to 330°C, and a second aliquot of 0.4 ml of the Se solution was swiftly injected to the flask. The temperature rapidly declined to 317°C, and the heating mantle was removed after 150 s of additional growth phase (Figure S3).

The obtained particles were precipitated by methanol, and isolated by centrifugation. Then, the precipitated nanocrystals were repeatedly washed by re-dissolution in toluene and precipitation in methanol. After the purifying procedure the nanocrystals were dissolved in toluene.



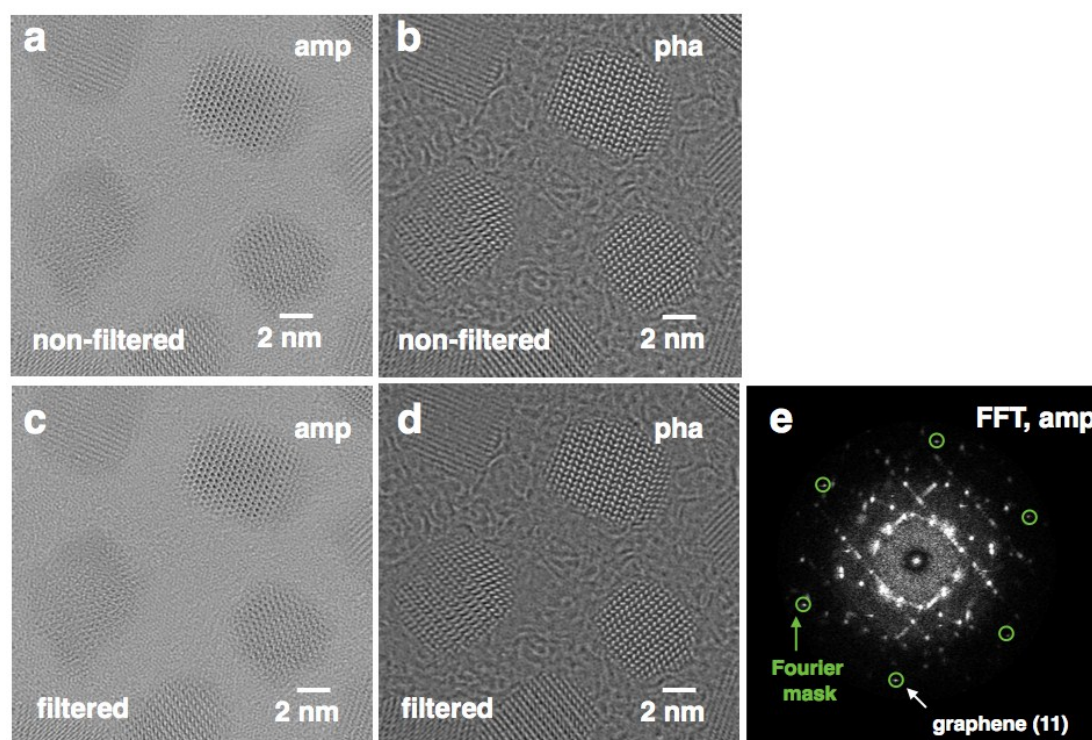
**Figure S3.** Schematic illustration of the double-injection CdSe synthesis procedure

#### *Preparation of TEM samples:*

The nanoparticles were precipitated from a toluene with methanol and re-dissolved in toluene. Then, a drop of the solution was placed on graphene TEM grids (CVD graphene film on Lacy carbon 300 mesh, Graphene Supermarket, NY, USA) and left to evaporate. The dried grids were cleaned with a custom-made apparatus combining gentle heating (50°C) and vacuum (10<sup>-7</sup> mbar) for 5 days under N<sub>2</sub> and kept in an inert atmosphere until mounting to the TEM.

### TEM measurements:

TEM measurements were performed using the spherical and chromatic double aberration-corrected FEI 60-300 Ultimate<sup>3</sup> ('PICO') at the Ernst Ruska-Centre, Germany. TEM images were acquired at 80 kV acceleration voltage with a spherical aberration value of  $-5 \mu\text{m}$  and a chromatic aberration value smaller than  $1 \mu\text{m}$ . Optimized phase contrast for TEM images was achieved at a slight overfocus of  $+5 \text{ nm}$  with a point resolution better than  $1.1 \text{ \AA}$ . Focal series reconstruction (FSR) was used to retrieve the phase of the electron exit plane wavefunction<sup>4</sup>. Experimental focal series were taken with an equidistant focal step of  $1.5 \text{ nm}$ , corresponding to about half the defocus spread of the microscope at the respective acceleration voltage. Twenty images were recorded around the negative spherical-aberration imaging (NCSI) defocus ( $+5 \text{ nm}$  in the conditions mentioned above) for the phase retrieval using the Brite/Euram focal series reconstruction (FSR) algorithms based on maximum-likelihood algorithms for nonlinear reconstruction<sup>4</sup>. The reconstructed wavefunction was Fourier-filtered to subtract the graphene layers background. For the average size and aspect ratio, 30-35 particles of each



sample were analyzed. The image in Figure 6 was not Fourier filtered.

**Figure S4.** Exit-plane wave data of CdSe@CdS particles. The data corresponds with the data shown in figure 3b in the manuscript. Amplitude and phase after correction of residual two-fold astigmatism ( $0.5 \text{ nm}$  at  $120^\circ$ ) and third-order coma ( $25 \text{ nm}$  at  $10^\circ$ ) (a,b). The amplitude of the exit-plane wave function shows faint contrast and non-perfect symmetry since the particles are not pure weak phase objects and slightly tilted with respect to the low-index zone axis. Amplitude and phase after application of a Bragg-filter (c),(d). A Bragg-filter was used to remove Fourier components originating from the graphene support lattice. Fast Fourier transform and Bragg-filter (e). The Bragg-filter mask removes only fine detail fringes in the wavefunction that is associated with the graphene (11) lattice spacing ( $1.24 \text{ \AA}$ ). The mask diameters are chosen narrow so that they do not overlap with Fourier components of the CdSe@CdS particles.

### ***Preparation of XRD samples:***

The nanoparticles in toluene were precipitated in methanol and re-dissolved in 0.5 ml of hexane. The solution was dripped onto a small Si wafer, and the solvent was evaporated on a heating mantle. Data were collected on Panalytical Empyrean Powder Diffractometer equipped with position sensitive (PSD) X'Celerator detector using Cu K $\alpha$  radiation ( $\lambda=1.5405 \text{ \AA}$ ) and operated at 40 kV and 30 mA. The usual Bragg-Brentano  $\theta/2\theta$  and grazing incident beam geometry were employed. The grazing incident scan was performed at a constant incident beam angle of  $2^\circ$  in a  $2\theta$  range of  $20^\circ$ - $60^\circ$  with a step of  $0.05^\circ$  and 2 s per step.

### ***Optical measurements:***

A small amount (0.1 ml) of sample was taken from each batch and diluted with toluene to an optical density of 0.1-0.2. UV absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer. Photoluminescence (PL) emission spectra were measured with a Shimadzu spectrofluorophotometer RF-5301pc.

### **References**

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2. Blackman, B.; Battaglia, D. M.; Mishima, T. D.; Johnson, M. B.; Peng, X., Control of the Morphology of Complex Semiconductor Nanocrystals with a Type II Heterojunction, Dots vs Peanuts, by Thermal Cycling. *Chemistry of Materials* **2007**, *19* (15), 3815-3821.
3. (a) Haider, M.; Hartel, P.; Mueller, H.; Uhlemann, S.; Zach, J., Information Transfer in a TEM Corrected for Spherical and Chromatic Aberration. *Microscopy and Microanalysis* **2010**, *16* (4), 393-408. (b) Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C) et al. FEI Titan G3 50-300 PICO. *Journal of large-scale research facilities* **2015**, *1*, A34.
4. (a) Coene, W. M. J.; Thust, A.; Op de Beeck, M.; Van Dyck, D., Maximum-likelihood method for focus-variation image reconstruction in high resolution transmission electron microscopy. *Ultramicroscopy* **1996**, *64* (1), 109-135; (b) Thust, A.; Coene, W. M. J.; Op de Beeck, M.; Van Dyck, D., Focal-series reconstruction in HRTEM: simulation studies on non-periodic objects. *Ultramicroscopy* **1996**, *64* (1), 211-230.