Supporting information

Binary Superlattices of PbSe and CdSe Nanocrystals

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Determination of the nanocrystal concentrations in TCE suspensions.

The concentration of the PbSe nanocrystals in suspension with TCE as a solvent was determined using the method proposed by Moreels et al.[1]. In this method, the concentration of nanocrystals in a suspension was measured by inductively-coupled plasma mass spectrometry (ICP-MS) combined with a TEM analysis of the size and shape of the nanocrystals. In a second step, the absorbance of the suspension was measured and related to the nanocrystal concentration. More specifically, they used the integrated absorbance $\int \mathbf{A} d\mathbf{E} = \int \mathbf{-\log (\mathit{I}/\mathit{Io})}\, d\mathbf{E}$ of the first exciton transition to determine the integrated molar extinction coefficient as a function of the nanocrystal diameter $\boldsymbol{d}$, yielding:

$$\boldsymbol{\varepsilon_{gap,\,eV} = 3.1\, d^{0.9}}\ (\mathrm{cm^{-1}\ \mu M^{-1}\ meV}) \qquad \text{(S1)}$$

By using the absorbance integrated over the inhomogeneously broadened first transition, effects of a variation in size-dispersion can be eliminated. We have determined the core diameter of the PbSe nanocrystals used in the crystallization experiments from TEM analysis (7.3 nm), and used this value to calculate $\boldsymbol{\varepsilon_{gap,\,eV}}$ from Eqn. (S1). From the absorbance (absorption spectrum presented in Figure S1) measured trough a suspension (thickness $\boldsymbol{l}$) of the PbSe nanocrystals in TCE we obtained the integrated absorbance and used this to determine the PbSe nanocrystal concentration $\mathbf{c}$ via the Lambert-Beer law: $\int \mathbf{A}\, d\mathbf{E} = \int \mathbf{-\log (\mathit{I}/\mathit{Io})}\, d\mathbf{E} = \boldsymbol{\varepsilon_{gap,\,eV}\, c\, l}$.

The concentration of CdSe nanocrystals in a TCE suspension was determined following the method of Yu et al.[2]. Yu et al. determined the molar extinction coefficient for CdSe suspension of known concentrations at the maximum of the first exciton absorption peak, yielding:

$$\boldsymbol{\varepsilon = 5857\, d^{2.65}}\ (\mathrm{cm^{-1}\ M^{-1}}) \qquad \text{(S2)}$$

In order to determine the concentration $\boldsymbol{c}$ of the CdSe nanocrystals in diluted TCE suspensions, we have measured the absorbance at the first exciton transition (absorption spectrum presented in Figure S2). The concentration of the diluted stock-suspension is then calculated from the Lambert-Beer law $\mathrm{A} = \mathbf{-\log (\mathit{I}/\mathit{Io})} = \boldsymbol{\varepsilon\, c\, l}$ and equation (S2), applied to nanocrystals with a core diameter d of 3.4 nm as obtained from TEM.

[1] Moreels, I.; Lambert, K.; De Muynck, D.; Vanhaecke, F.; Poelman, D.; Martins, J.C.; Allan, G.; Hens, Z. *Chem. Mater.* **2007,** *19,* 6101–6106.
[2] Yu, W.W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003,** *15,* 2854-2860.

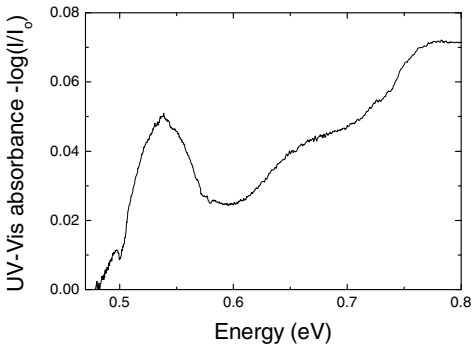

Figure S1 Absorption spectrum of a PbSe nanocrystal suspension in TCE.

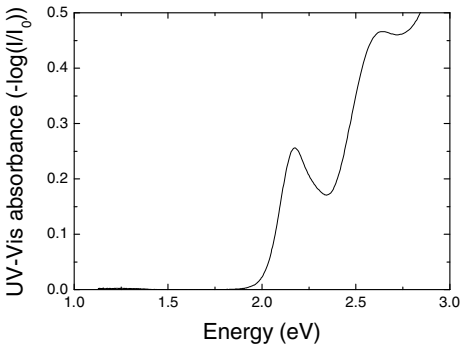

Figure S2 Absorption spectrum of a CdSe nanocrystal suspension in TCE.

Sample Preparation

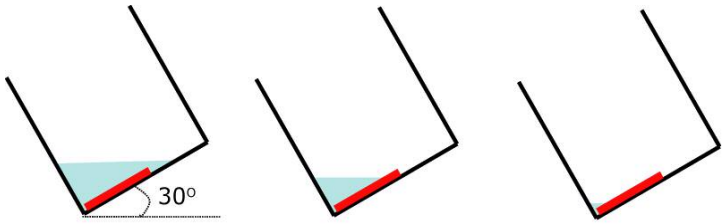

Figure S3: Schematic representation of the binary nanocrystal formation. Left: a TEM grid (copper) is placed in a mixed CdSe NC / PbSe NC suspension in a vial with the substrate forming an angle of 30º with the surface of the drying dispersion. Centre: evaporation of the solvent from the suspension under reduced pressure at 70 ºC. Right: the solvent is evaporated, the binary structures are formed on the TEM grid.

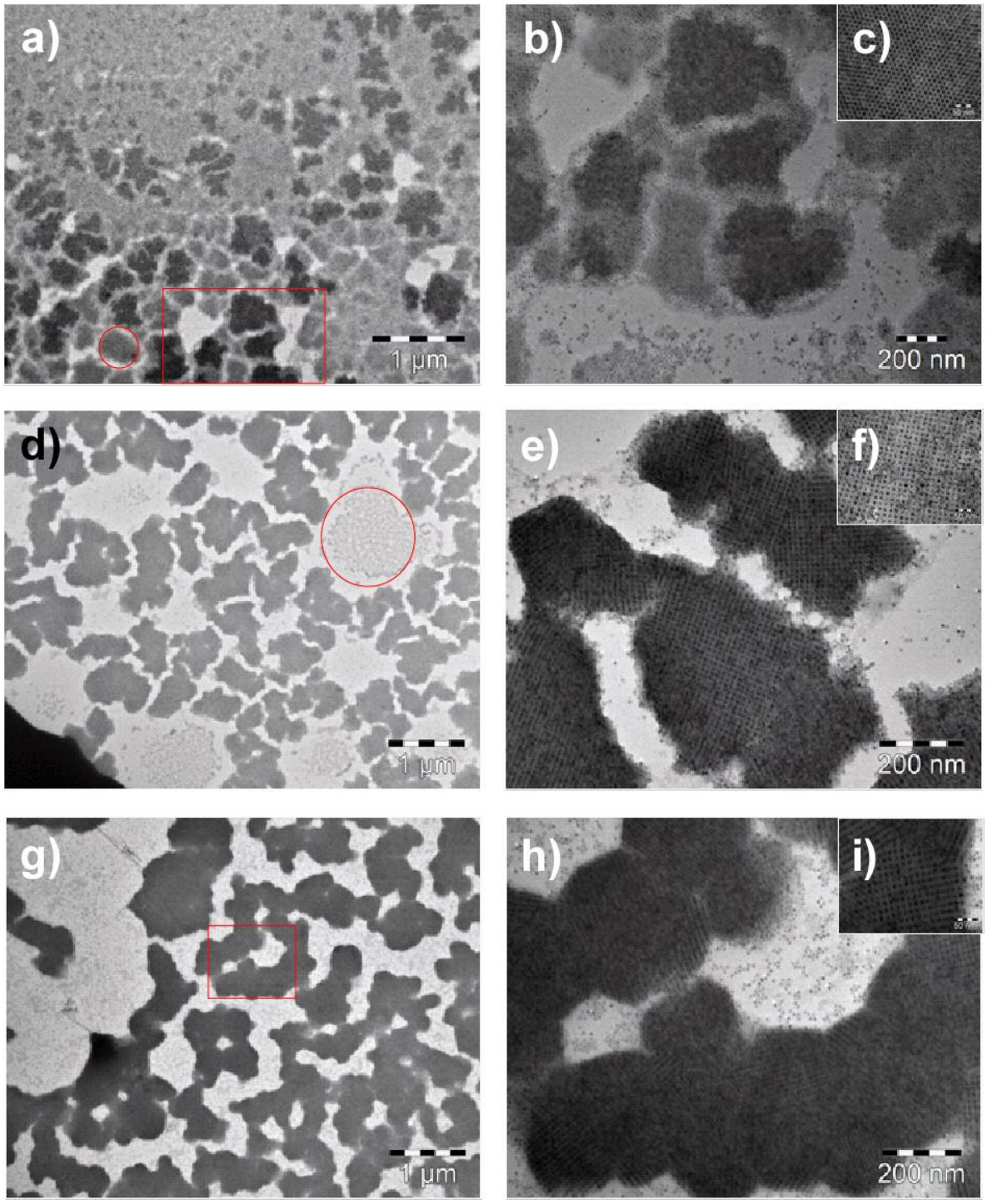

Figure S4. Low resolution TEM overview of the surface coverage of CdSe (core-diameter 3.4 nm) and PbSe nanocrystals (core-diameter 7.3 nm).with (a) a concentration ratio CdSe/PbSe of 4. The dark colored regions on the TEM substrate are AB_2 structures. One of the few AB_{13} structure was found in the area at the position of the circle. The area in the top of the TEM image (light gray) is predominated by disorder and large CdSe superlattices. An enlarged view in the region of the rectangle is shown in (b) with mainly AB_2 structures as is shown in the inset, (c).

In (d) a TEM image with a concentration ratio CdSe/PbSe of 5.5 shows mostly AB_{13} structures (darker regions) as the enlargement of (e) and (f) shows. Besides disordered structures (see red circle), empty regions and CdSe superlattices are found. Note that the edges of the separated AB_{13} domains show similar features indicating that originally larger AB_{13} domains were present, which were probably broken during the drying process. At this particular position on the TEM image, no AB_2 structures are found, however at different areas on the TEM grid, they were observed.

In (g) a TEM image is shown, obtained with a concentration ratio CdSe/PbSe of 11 in suspension. Large domains of cub-AB_{13} (dark regions) are observed as the enlarged view in (h) and the inset in (i) shows. At this concentration ratio, the structures increased in height compared to AB_{13} structures observed for a concentration ratios of 5.5. The preferential crystal orientation is the (100) plane parallel to the substrate with a minor fraction of the lattices showing the (110) plane parallel to the substrate.

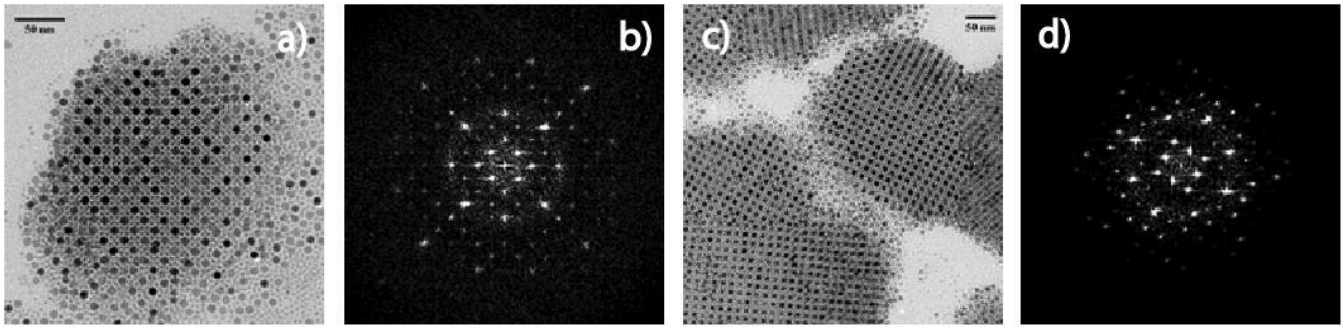

Figure S5. High resolution TEM images of the AB_{13} structures build from CdSe (core-diameter 3.4 nm) and PbSe nanocrystals (core diameter 7.3 nm). (a) a single crystal of AB_{13} surrounded by a disordered deposit, (b) it's Fourier transform. (c) larger overview TEM image of different domains of AB_{13} with different crystallographic orientations, (d) FFT from a region in the upper right corner with the (110) plane parallel to the substrate.

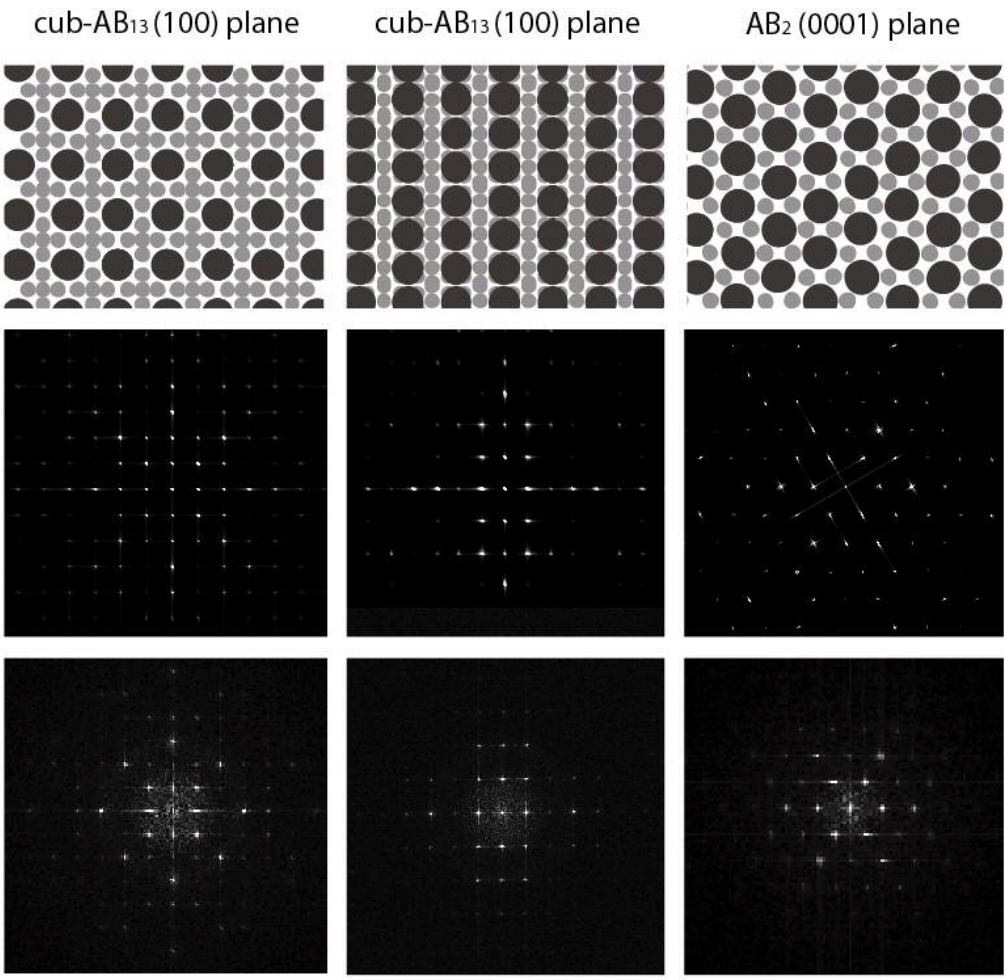

Figure S6: Comparison between the Fast Fourier Transforms (FFT) of the obtained AB_2 and AB_{13} superlattices and model structures. Top: model planes; Centre: their FFT; Bottom: the experimentally obtained FFT.