Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting information

Colloidal PbS quantum dot stacking kinetics during deposition via printing

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Experimental section

Synthesis of colloidal PbS quantum dots: The synthesis method was following previous literature with slight modifications, briefly described as follows:[10] 1.1 g PbO powder was loaded into a three-necked flask mixing with 7 mL oleic acid ($C_{18}H_{34}O_2$, OA) and 20 mL octadecene ($C_{18}H_{36}$, ODE). The mixture was degassed three times, with alternatively injecting pure argon (Ar), then heated up to 150 °C to obtain a transparent $Pb(OA)_2$. The temperature of the mixture was decreased back to 100 °C and a degassing process for 6 hours was performed to completely remove the inner moisture and the organic solvent with a low-boiling point. Ar was injected with stop degassing simultaneously and the temperature was decreased to 80 °C. 530 µL bis(trimethylsilyl)sulfide ($(TMS)_2S$, was injected in $Pb(OA)_2$ solvent to initiate the nucleation and growth of PbS QDs. The reaction was last for 90 s and the flask was cooled down immediately by an ice-bath, simultaneously, 10 mL octane was injected into the flask to terminate to the reaction. The acetone was used to purify the QDs by high-speed centrifugation. QDs were then re-dispersed in octane with a concentration of 50 mg/mL for the printing deposition. To fit the potential practical applications, the ZnO compact layer coated glass slides were used as the substrates for the printing of the QDs.

Printing of QDs: The printing of QDs was performed with a home-made slot-die coater, which had a fixed printer head with a 25 mm wide solvent-flow-guider, a microfluidic syringe pump, a substrate holder and a computer control. To initialize the deposition, the injection rate of QDs was set at 100 µL/min and the height of the flow-guider measured from the substrate was set to 0.5 mm. When the solvent flew out along the flow-guider, the substrate holder was moving with the rate of 3 mm/s along the printing direction simultaneously. The deposition was terminated when the sample holder reached a preset position and the injection was stopped simultaneously with the print-head rising for 0.5 mm to avoid reflux of residual solution. A QDs film was achieved when the solvent was fully dried. Notably, QDs were directly printed on the ZnO layer in the following steps. The film homogeneity and flatness were checked by GISAXS scanning along the printing direction before printing and the in-situ observation as seen in Fig. S2(c) and 2(d). The ZnO coated ITO/Glass was also used for the deposition of QDs as a reference sample. The corresponding GISAXS data of QDs on ZnO/ITO/Glass is shown in Fig. S6. It shows similar scattering features as the GISAXS data of QDs/ZnO/Glass sample.

In situ GISAXS measurement: The printer was installed in the beamline P03 of the Deutsches Elektronen-Synchrotron (DESY) in Hamburg. The complete printing set-up was fixed on a hexapod that was responsible for the alignment and scans. The X-ray photon energy was 12.9 keV corresponding to the wavelength of 0.96 Å. The Pilatus 1M was used as GISAXS detector with a sample-detector distance of 2591 nm, which was further calibrated by AgBeh. The incident angle was set to 0.4° which was higher than the theoretical critical angles of Si/SiO_x, ZnO and bulk PbS materials based on scattering length density calculations. The alignment of the substrate was performed before the in-situ experiment and an X-ray scan was performed to localize a uniformed and smooth region (with a length of 3 mm, which is divided into 15 points) on the substrate for the in-situ observation afterward. The in-situ monitoring started immediately after the sample holder stopped moving. The first single GISAXS measurement on the as-deposited QD film was close to the printer head and close to the fresh deposition region. The duration of the single GISAXS measurements was set to 0.1 s and realized by the fast-shutter. The setup then moved to the next point in another 1.9 s for the next single GISAXS measurement. The evaporation of the solvent and the film drying were quite fast (30 s), as confirmed by the time-resolved 2D GISAXS data.

The simulations and calculations: The 2D GISAXS data simulations were performed with the software BornAgain (version 1.61).[S1] The scattering functions of simulated materials were all based on their scattering length density. The QDs with a uniformed diameter of 2.88 nm were modeled by a hard sphere with selected inter-distance. The layout of the assembly of QDs was described by a hexagonal 2D lattice. The superlattice-diffraction calculations were based on the GIXSGUI package (version 1.7.1) on the MATLAB platform.[S2]

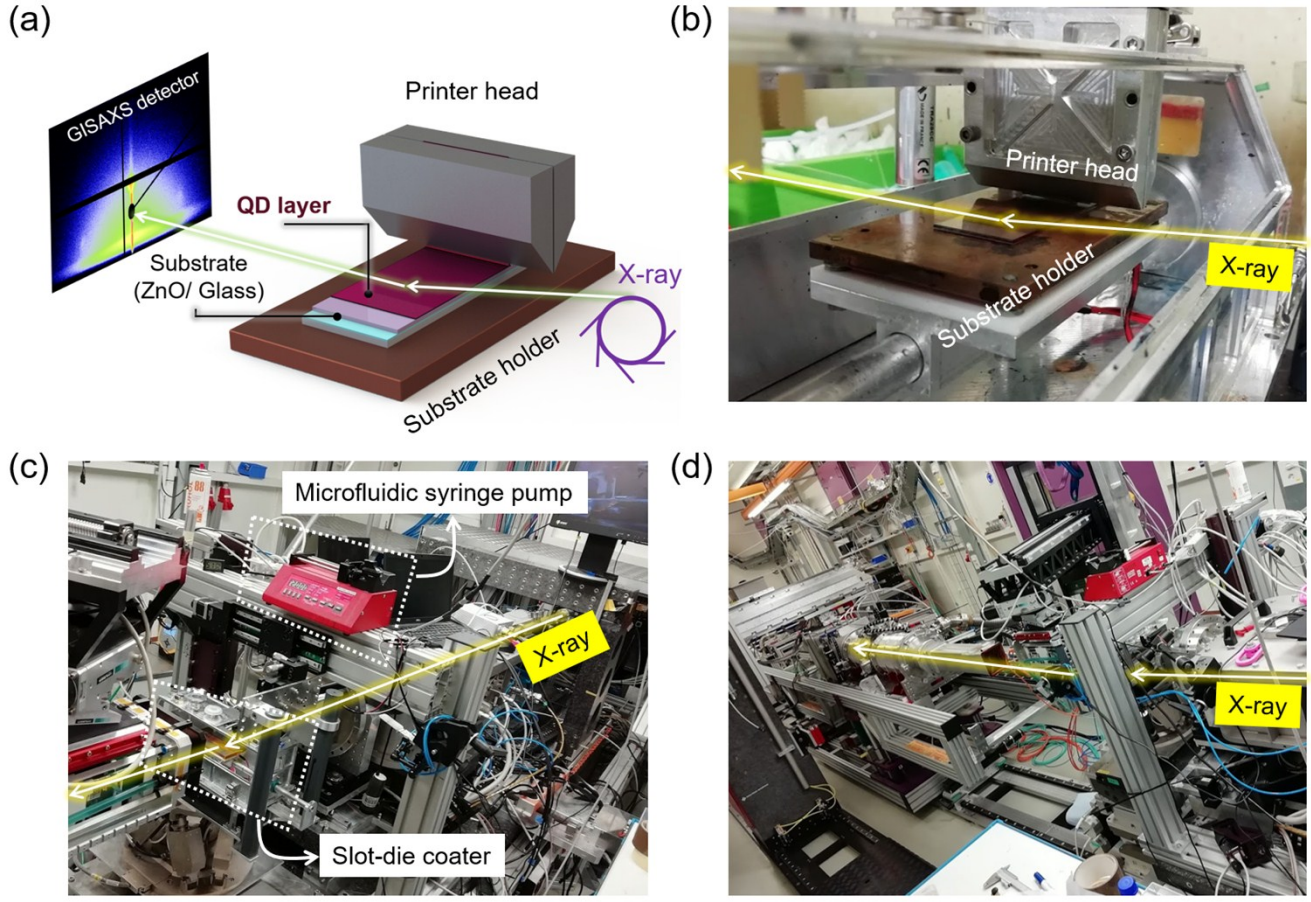

Fig. S1. Schematic (a) of the in-situ set-up used for printing and (b) the corresponding photograph with print head and substrate holder as indicated (X-ray beam is sketched for clarity). (c, d) Photographs of the integration of the slot-die coater in the experimental station P03.

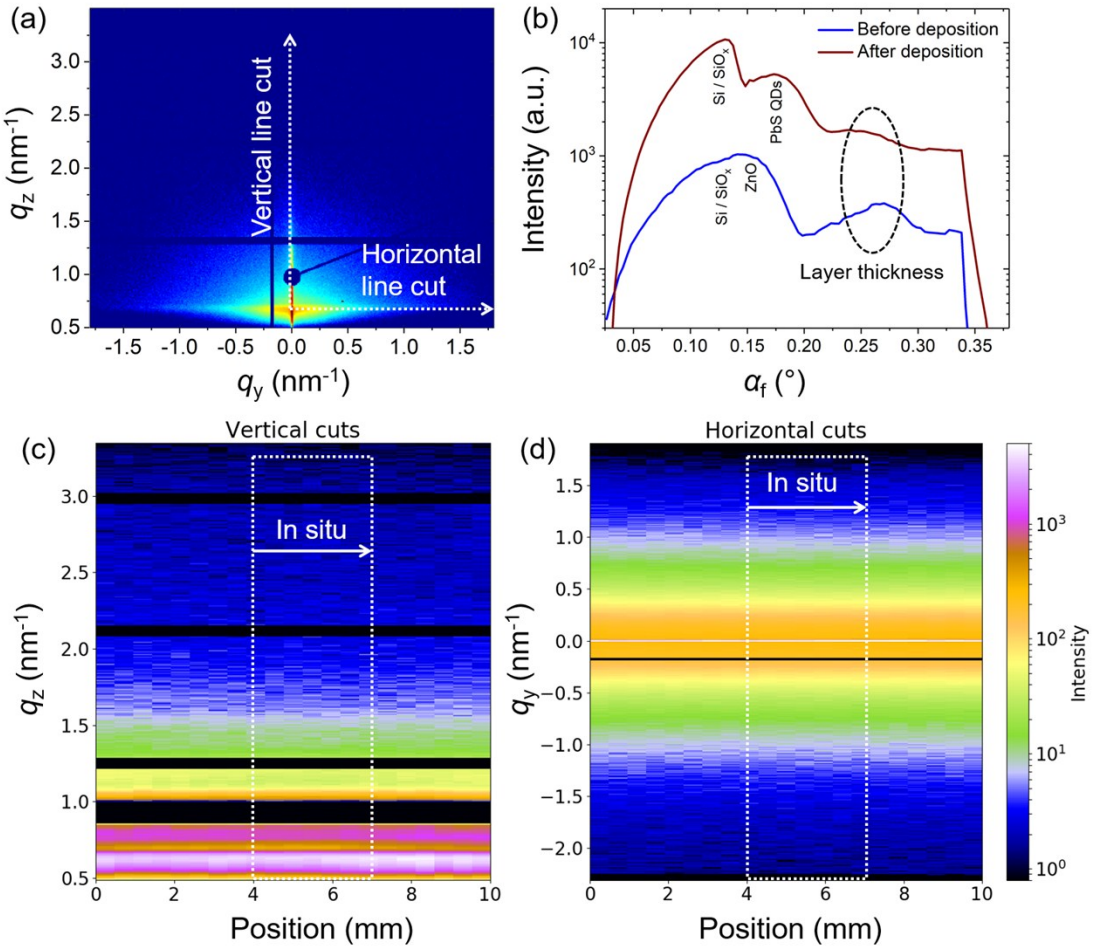

Fig. S2. (a) 2D GISAXS pattern of ZnO coated glass substrate with the schematics for the vertical and horizontal line cuts. (b) Vertical line cuts of 2D GISAXS data before (blue) and after (red) deposition of the QDs as function of the scattering angle α_f with Yoneda peak positions of the involved materials as calculated from the corresponding scattering length density values. The intensity modulation in the angular range 0.25° < α_f <0.3° resembles the ZnO (blue) and PbS (red) layer thickness. Mapping of (c) vertical and (d) horizontal line cuts of the 2D GISAXS data of the ZnO coated glass substrate. The range selected for the in situ experiment is highlighted in dashed box.

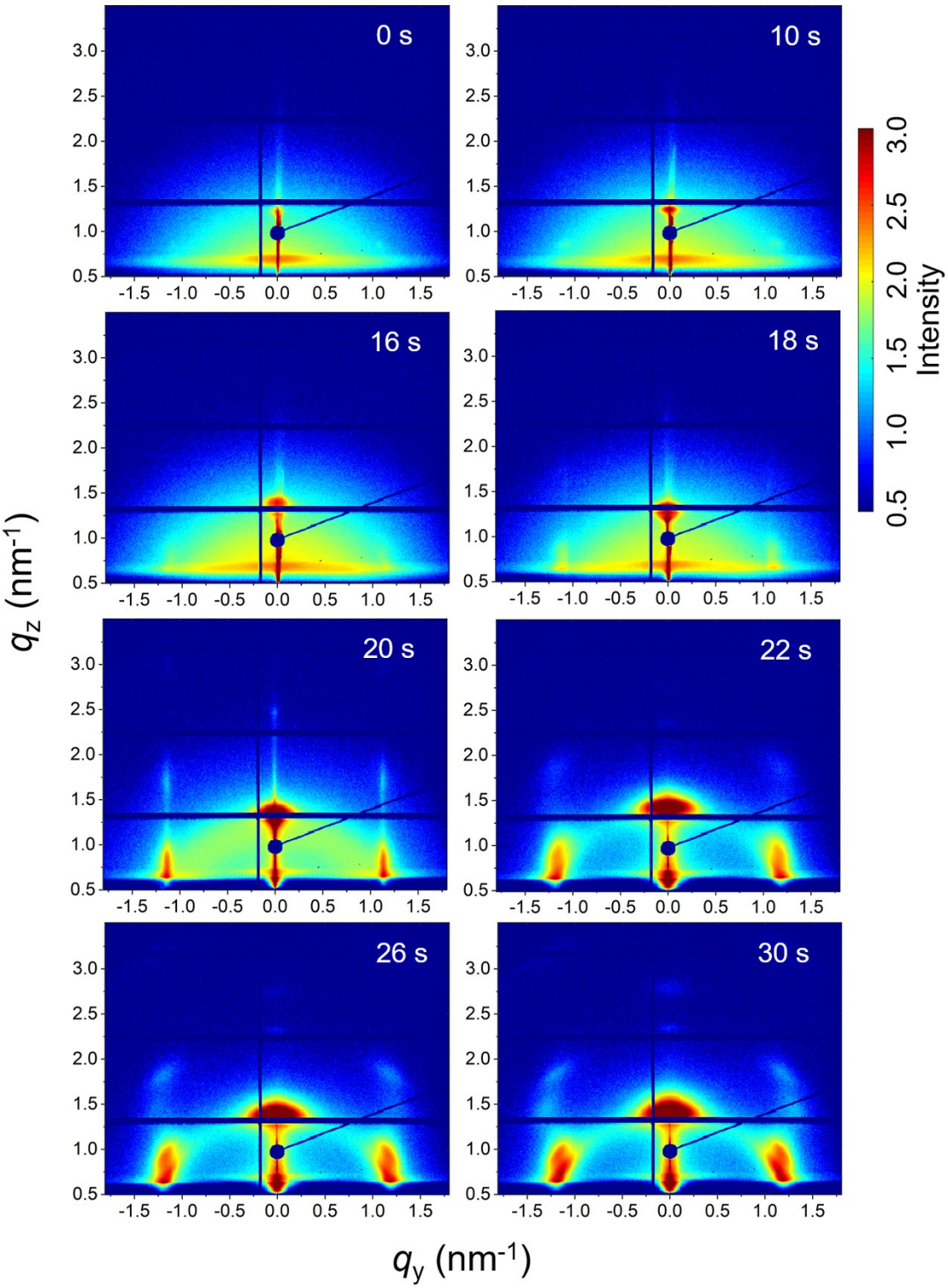

Fig. S3. Selected 2D GISAXS data at different times after deposition as indicated.

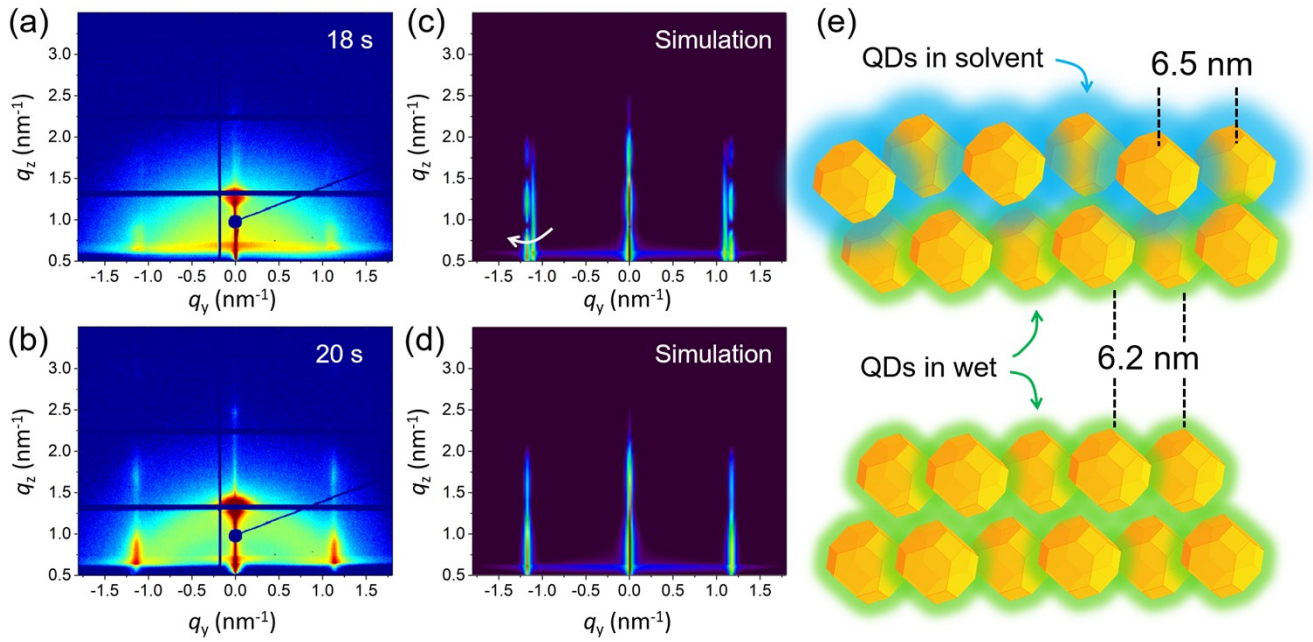

Fig. S4. (a,b) 2D GISAXS data and (c,d) respective simulated 2D images with BornAgain at (a,c) t = 18 s and (b,d) t = 20 s describing a templated stacking behavior of QDs. In the BornAgain simulation, a lattice length of 6.5 nm and 6.2 nm in a hexagonal layout is used to describe the scattering peaks at small and larger q_y values, respectively. (e) The corresponding schematics for describing the changes of inter-dot distances at t = 18 s (top) and t = 20 s (bottom).

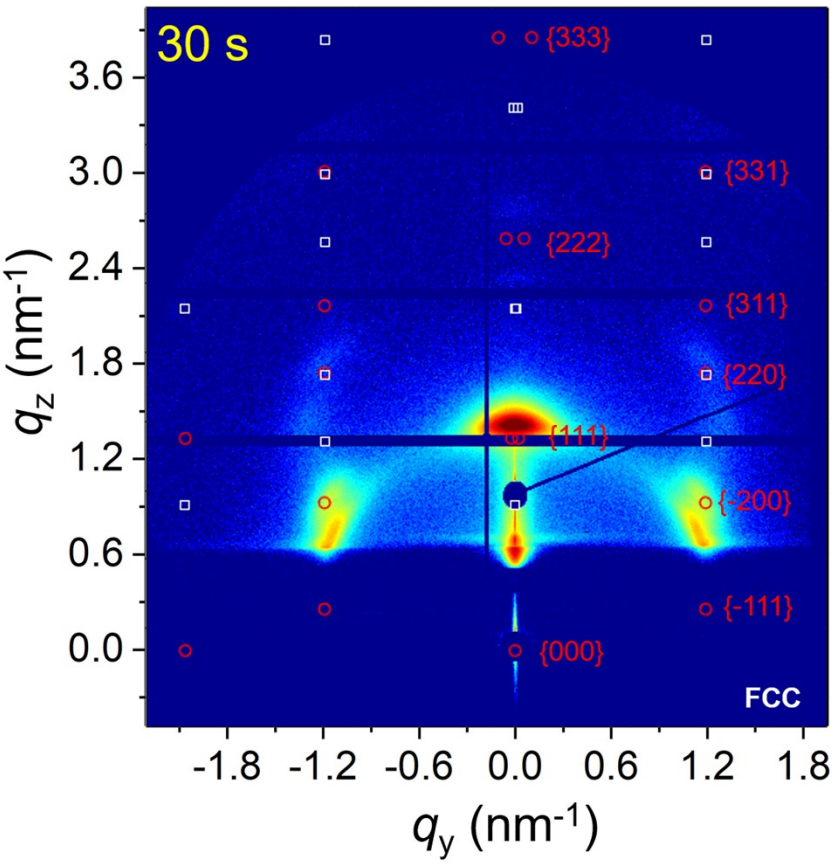

Fig. S5. 2D GISAXS image of printed film at t = 30 s with predicted Bragg peak positions as indicated with white (reflected) and red (diffracted) points based on the FCC superlattice calculation with lattice parameters $a = b = c$ = 8.6 nm and $\alpha = \beta = \gamma = 90°$.

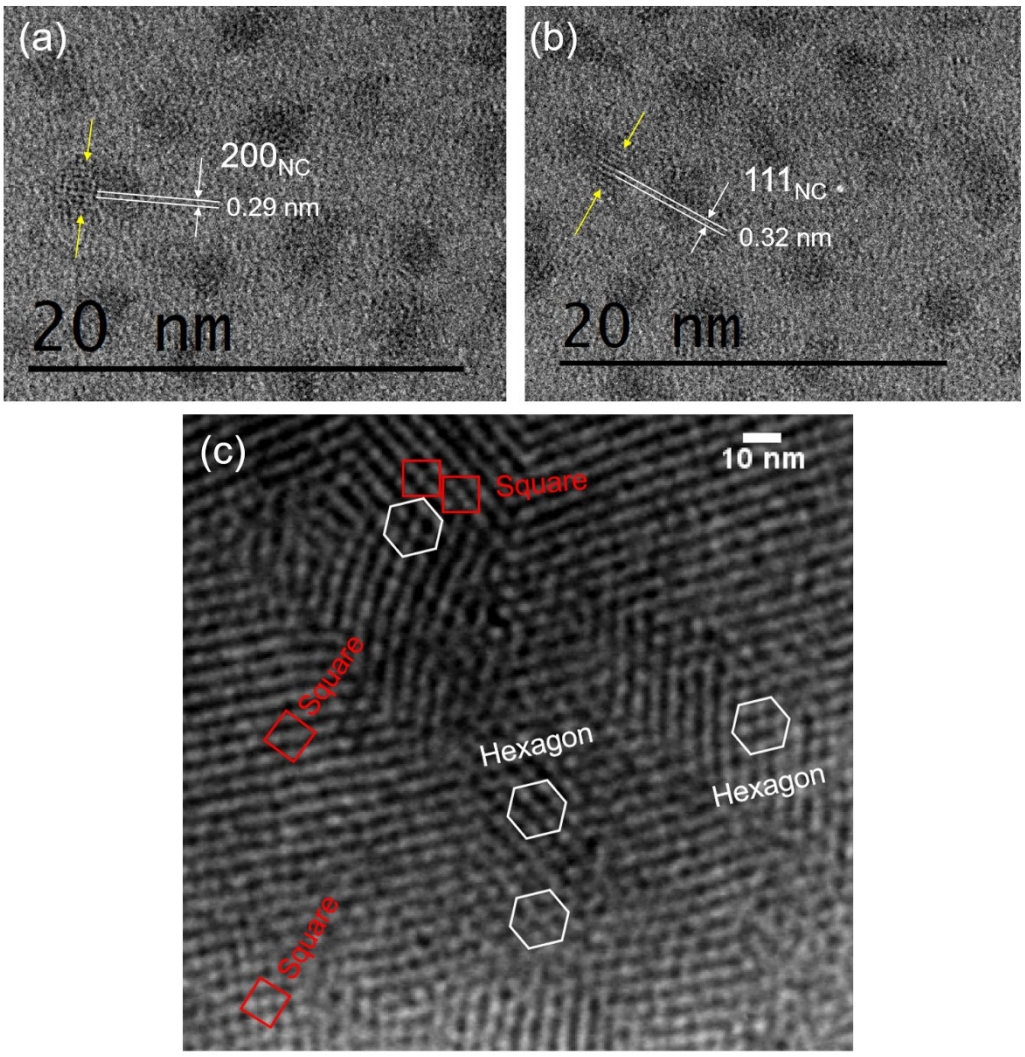

Fig. S6. High-resolution TEM images showing the (a) $(200)_{NC}$ plane and (b) $(111)_{NC}$ plane of the used PbS QDs. The corresponding lattice distances are 0.29 ± 0.01 nm and 0.32 ± 0.01 nm, respectively, as measured over 5 lattice fringes. (c) TEM image of printed QD film on a carbon film (on a copper grid). The red squares indicate the $(110)_{SL}$ plane in the BCC superlattice and the white hexagons indicate the $(111)_{SL}$ plane in the FCC superlattice.

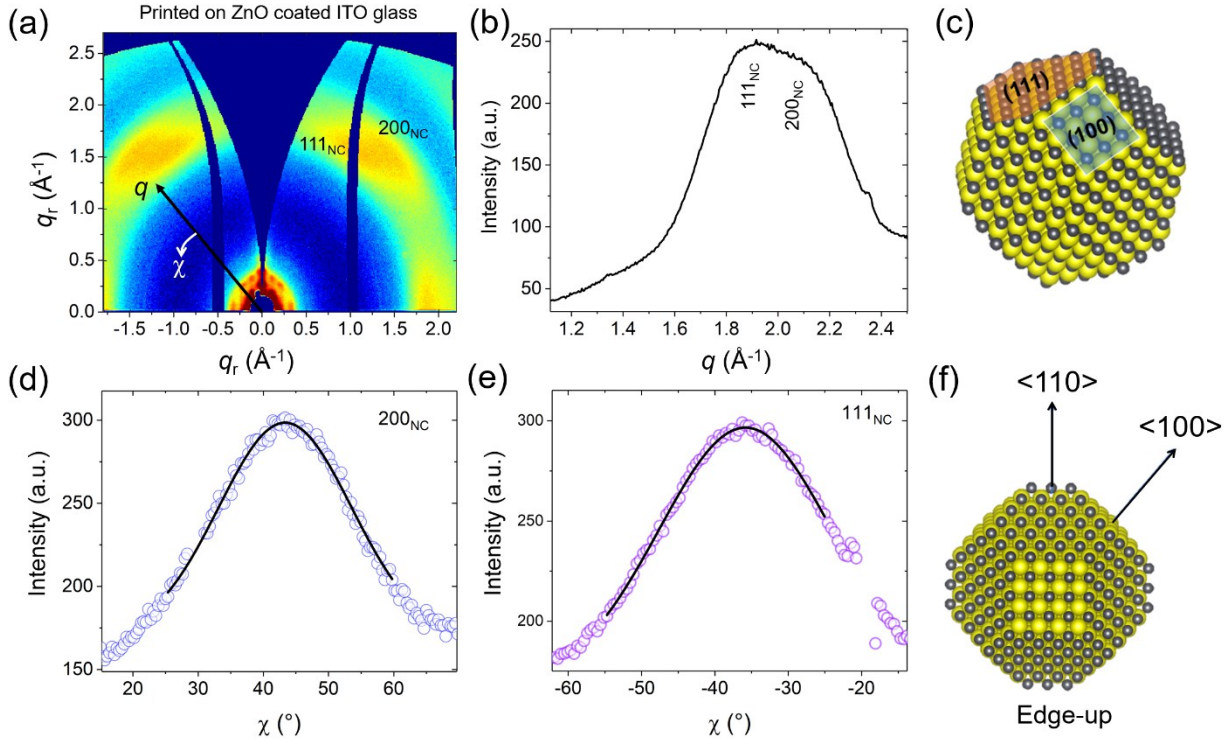

Fig. S7. (a) 2D GIWAXS data of printed PbS QD superlattice solids on ZnO coated glass. (b) Azimuthal integration of the 2D GIWAXS data along q showing the 200_{NC} and 111_{NC} Bragg peak contributions and (c) schematic of corresponding facets on a PbS QD with $(200)_{NC}$ plane and $(111)_{NC}$ plane. Orientation distribution of (d) 200_{NC} and (e) 111_{NC} Bragg peaks. (f) Sketch of the final facet orientations of PbS QDs in the final array, which is described as edge-up.

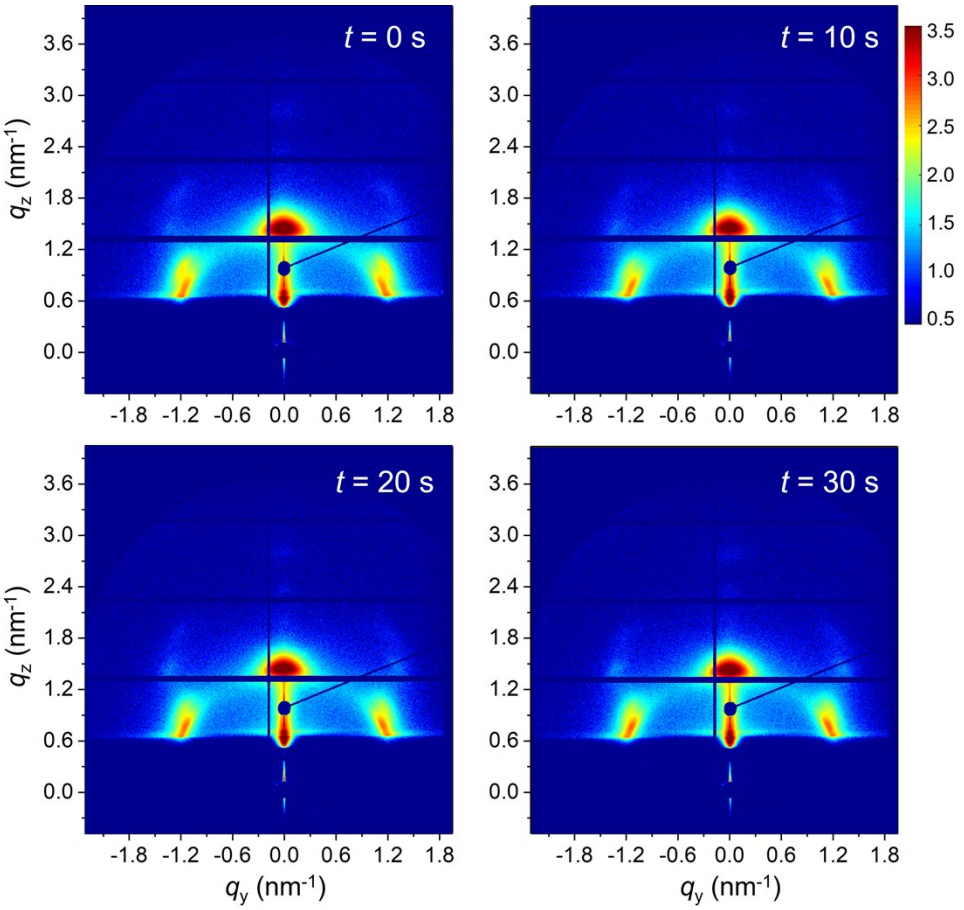

Fig. S8. 2D GISAXS data from the beam damage check performed after the X-ray measurement. The GISAXS data are taken at exactly the same positions corresponding to the GISAXS in situ measurements during the printing at times as indicated.

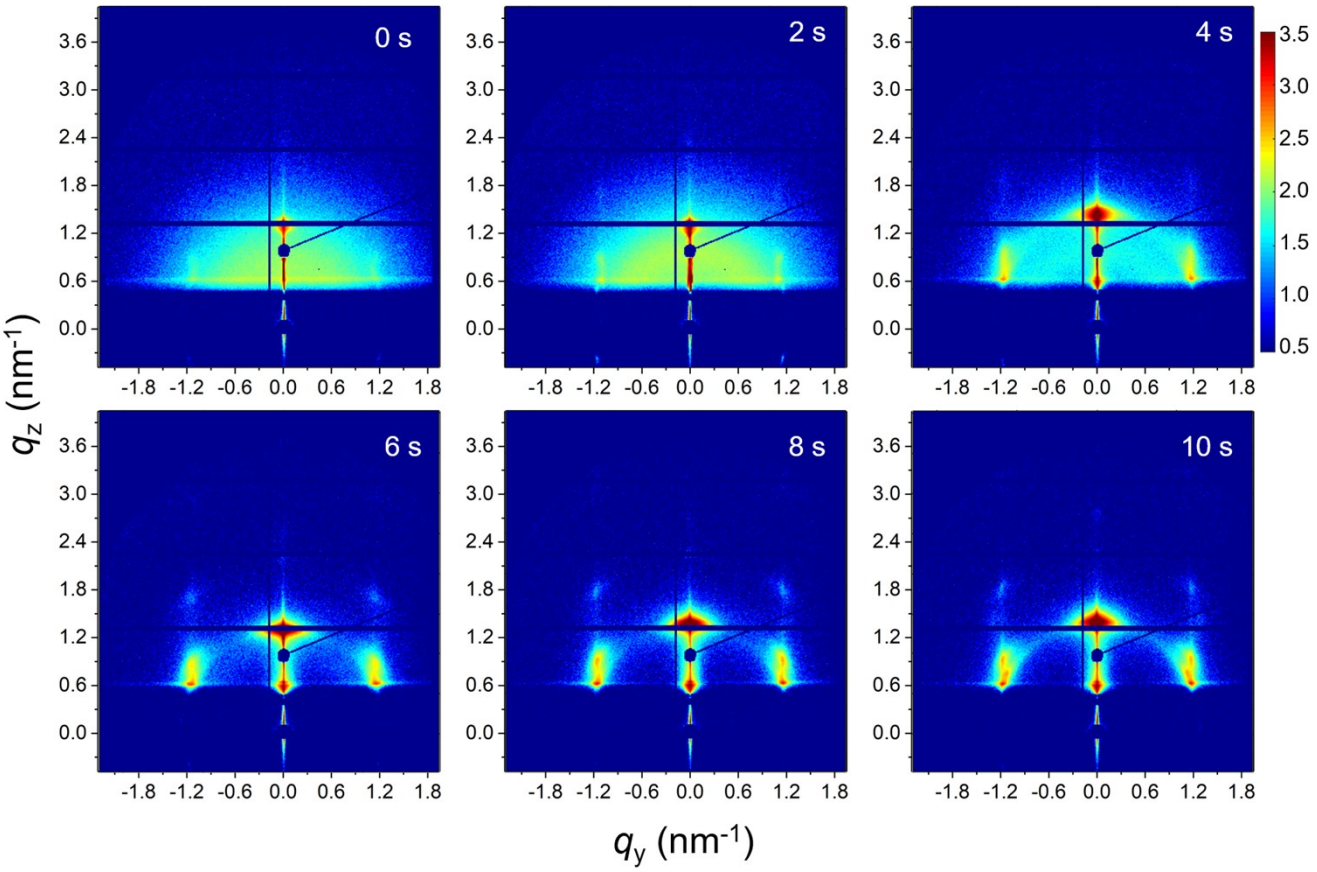

Fig. S9. 2D GISAXS data of QDs film deposited on a different substrate (ZnO/ITO/glass) by printing with the same protocol as used for the printing on ZnO/glass substrate at times as indicated. Times are not exactly compatible with the printing experiment described in the main manuscript due to additional alignment before the measurement. The observed superlattice structure evolution indicates similar QD stacking kinetics.

References:

[S1] G. Pospelov, W. Van Herck, J. Burle, J. M. Carmona Loaiza, C. Durniak, J. M. Fisher, M. Ganeva, D. Yurov and J. Wuttke, *J. Appl. Cryst.*, 2020, **53**, 262-276.

[S2] Z. Jiang, *J. Appl. Cryst.,* 2015, **48**, 917-926.