

# **Three-Dimensional Nanocrystal Superlattices Grown in Nanoliter Microfluidic Plugs**

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## Experimental section

**Chemicals.** tetrachloroethylene, 1-dodecanethiol (98%), gold (III) chloride trihydrate (99,9%), diethyl ether (anhydrous,  $\geq 99,7\%$ ), benzene (ACS reagent,  $\geq 99\%$ ), triphenylphosphine (99%), borane tert-butylamine complex (97%), oleic acid (90%), octadecene (90%), iron (III) chloride hexahydrate (97%), sodium hydroxide, trioctylphosphine oxide (99%), tetradecylphosphonic acid (99%, Polycarbon), octadecylphosphonic acid (99%, Polycarbon), selenium (powder, 99.99%), lead acetate trihydrate (99,999%), squalane (99%), toluene, tetrachloroethylene (TCE), ethanol, isopropanol, butanol were purchased from Sigma-Aldrich. Cobalt chloride anhydrous (99,7%) was purchased from Alfa Aesar. Dimethylcadmium (97%), trioctylphosphine (97%) were purchased from Strem. (Tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1 trichlorosilane was purchased from United Chemical Technologies. FC-40 (a mixture of perfluoro-tri-*n*-butylamine and perfluoro-di-*n*-butylmethylamine) and FC-70 (perfluorotripentylamine) were purchased from 3M. All chemicals were used as received without additional purification.

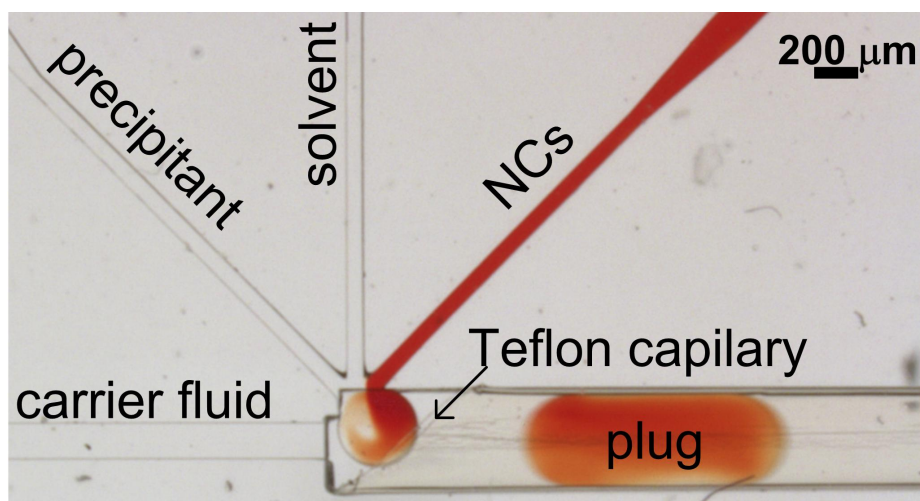
**Nanocrystal Synthesis.** *Synthesis of PbS NCs* capped with oleic acid was performed from lead oleate and bis-(trimethylsilyl)sulfide according to the Ref.<sup>1</sup> *CdSe NCs* were synthesized in a hexadecylamine/trioctylphosphine oxide/trioctylphosphine mixture using dimethylcadmium and TOPSe according to Ref.<sup>2</sup> The *synthesis of CoFe<sub>2</sub>O<sub>4</sub> NCs* was carried out by high temperature decomposition of mixed iron(III)/cobalt(II) oleate at 320 °C in the presence of oleic acid as the stabilizing agent.<sup>3</sup> Dodecanethiol stabilized 7 nm *Au NCs* were synthesized as described in Ref.<sup>4</sup>: 0.25 mmol (124mg) of AuPPh<sub>3</sub>Cl and 0.125 mL of dodecanethiol were dissolved in 20 mL benzene and heated to 80° C under airless conditions. 2.5 mmol (0.217mg) of borane tert-butyl complex was added to mixture and heating continued for 30 min. The reaction mixture was cooled and Au NCs were washed with ethanol/toluene mixture. NCs were stored in chloroform. AuPPh<sub>3</sub>Cl precursor was prepared by mixing 0.2 g HAuCl<sub>4</sub>·3H<sub>2</sub>O and 0.254 g triphenylphosphine in 6 mL anhydrous ethanol under airless conditions. White

precipitate formed in 30 min. This precipitate was washed by ethanol and diethyl ether followed by drying under vacuum. Dodecanethiol stabilized 3.4 nm *Pd NCs* were synthesized as described in Ref.<sup>5</sup>

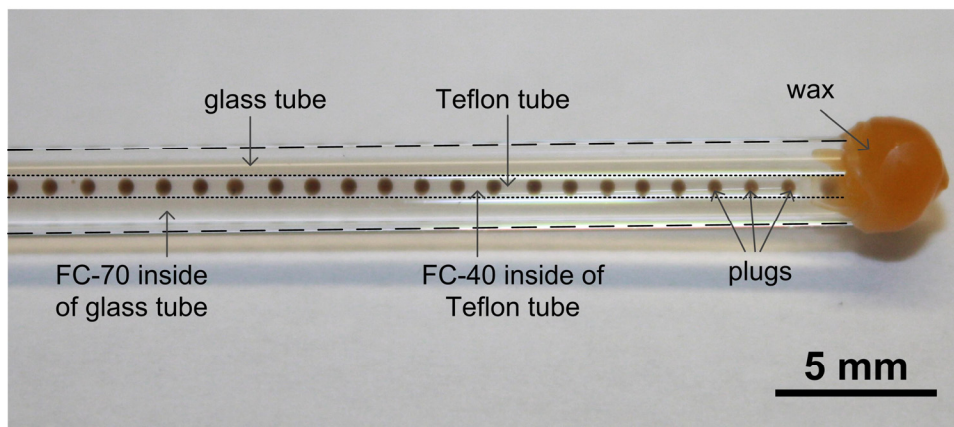
**Growth of colloidal crystals.** The microfluidic PDMS-devices (Figure S1) with four or five inputs were fabricated as described in Ref.<sup>6-8</sup> The microchannel surface of PDMS-device was functionalized first with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane and then coated with with amorphous fluoropolymer solution (Poly(4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene)),<sup>9</sup> to make PDMS-surface hydrophobic and compatible with organic solvents. Sample preparation was performed in according to the procedures described previously.<sup>8</sup> Teflon tube (400  $\mu\text{m}$  diameter, 50  $\mu\text{m}$  thick walls,  $\sim$ 25 cm of length) was inserted into the output microchannel of the device and their junction was sealed with capillary wax. FC-40, neat solvent, non-solvent and colloidal solution of NCs were loaded into 50-100  $\mu\text{L}$  Gastight syringes with 27-gauge needles and 30-gauge Teflon tubing. Injection of non-polar solvents into fluorinated carrier fluid led to the formation of droplets (plugs). Infusion syringe pumps controlled with LabView program were used to vary the composition of plugs. After tube was filled with plugs, its ends were sealed with wax in a glass tube filled with FC-70 to prevent evaporation of solvents from plugs. The samples were incubated and monitored within 5-10 days by optical microscope. After complete growth of colloidal crystals, crystals were floated out onto silicon substrate and studied with scanning electron microscopy (SEM). For kinetic studies, to overcome the problem of plugs moving and merging we prepared the plugs with elongated shape. To achieve this, we first generated plugs in 600  $\mu\text{m}$  diameter tubing which were then pushed into a smaller diameter tubing (400  $\mu\text{m}$ ). The plugs were longitudinally compressed into elongated ones.

Experiments with evaporation of solvents from plugs were performed without the use of PDMS-devices. Thin-wall Teflon tube (500  $\mu\text{m}$  of diameter) was connected directly to the 50-ml syringe through 27-gauge needle. Colloidal solution of NCs with toluene or TCE as solvent and FC-40 were alternatively sucked into the tube. The ends of Teflon tube were sealed with capillary wax and samples were left under open air to let solvent evaporate through the walls of Teflon tubing.

**Structural characterization of colloidal crystals.** Optical images were obtained using Leica MZ16 optical microscope. Scanning electron microscopy (SEM) images were obtained using FEI Nano SEM microscope operated at 20 kV. To prepare SEM samples, the plugs with colloidal crystals were floated out into isopropanol or ethanol drop on a Si-substrate, followed by washing with acetone and ethanol. To improve the quality of SEM images, it was necessary to completely remove traces of all solvents by heating samples at 70-80°C under vacuum for 10-12 hours. TEM images were obtained using FEI Technai3F microscope operating at 300kV acceleration voltage. The TEM images were compared to the projections simulated using Crystal Maker1.4 software package. To make samples for TEM-study, precipitates were pushed into isopropanol, sonicated and dropped onto TEM grids.

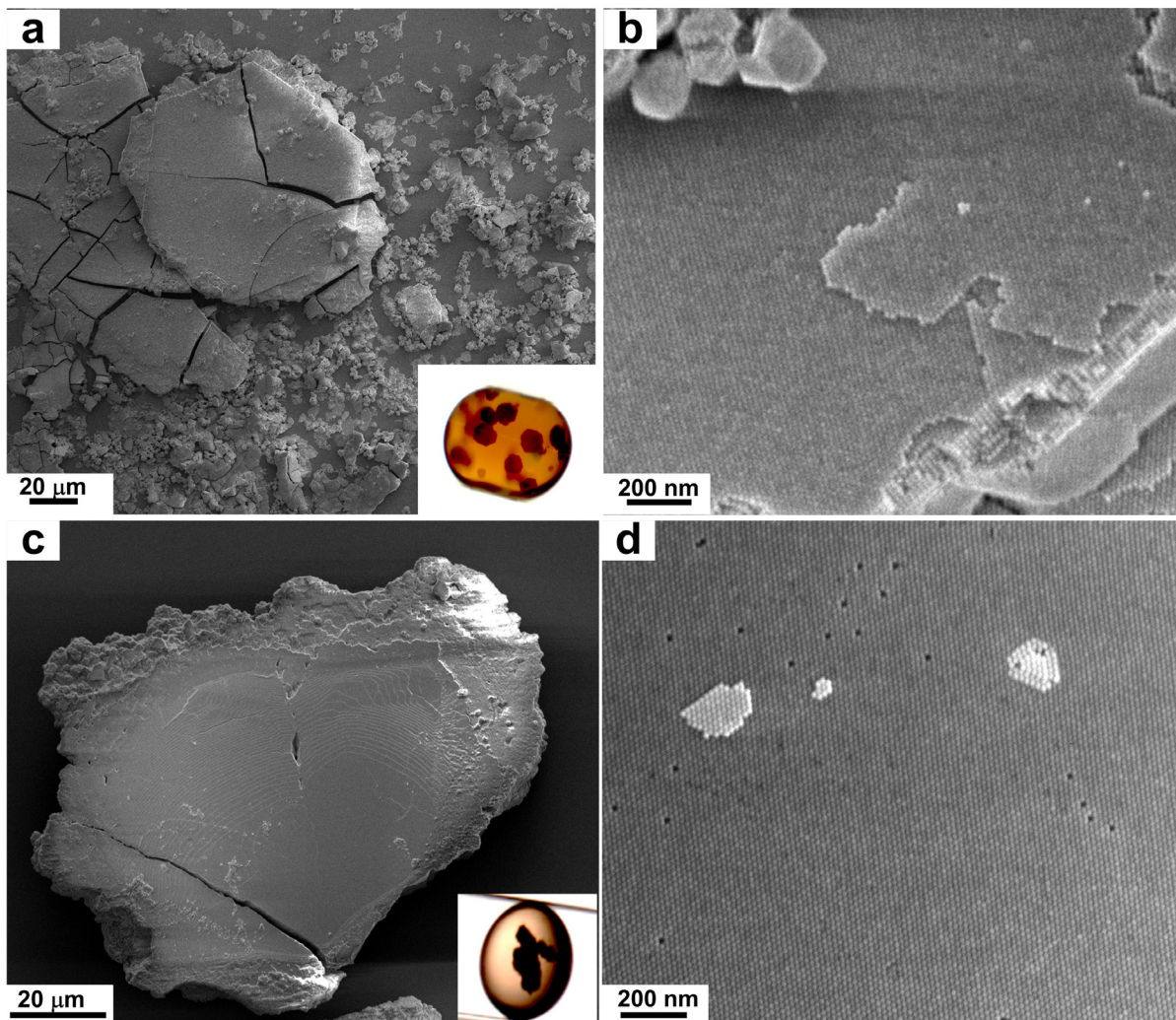


**Figure S1.** Magnified optical image of the PDMS device during experiment.

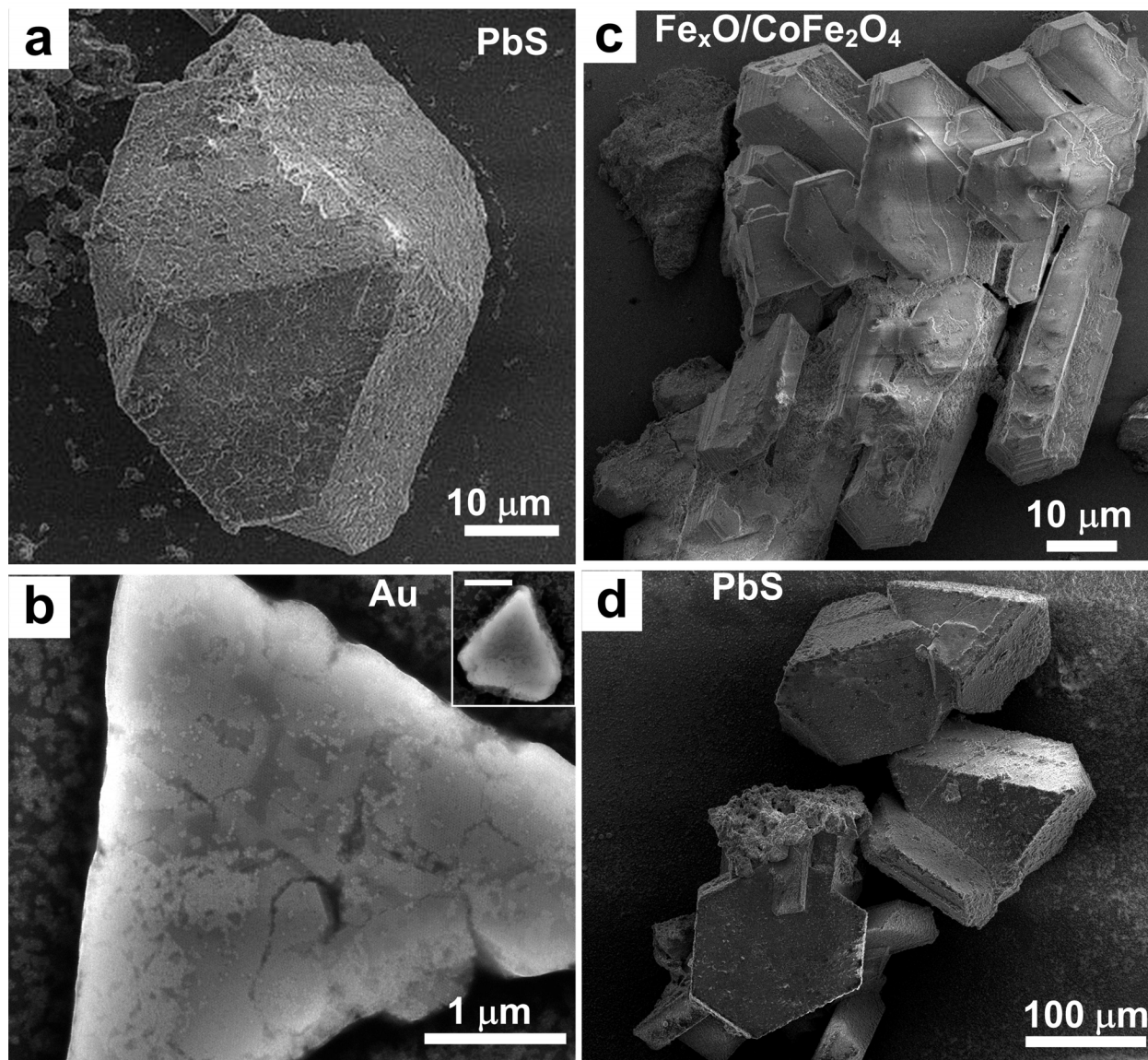


**Figure S2.** Incubation of the microfluidic plugs in sealed capillary.

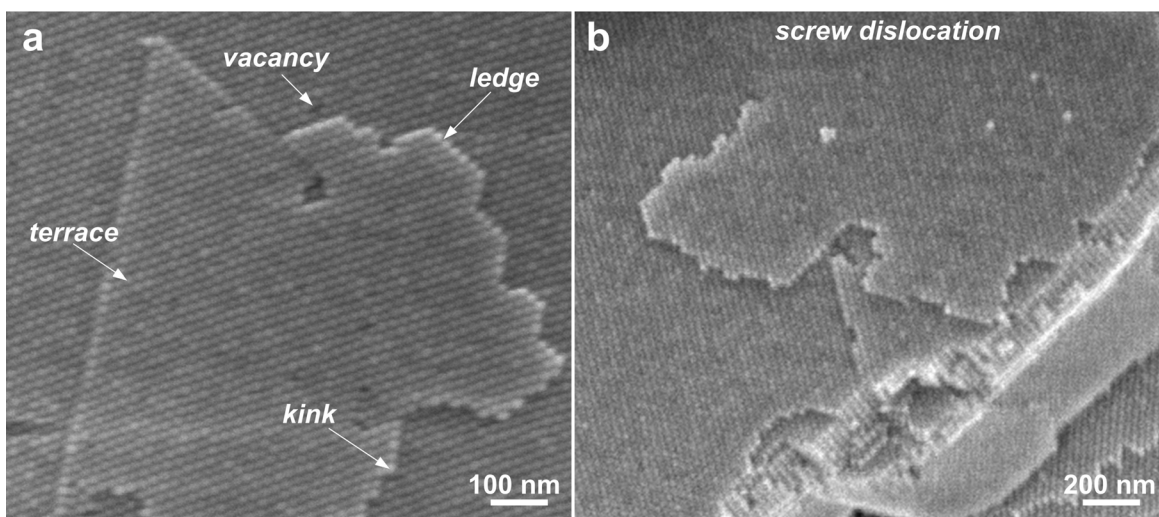




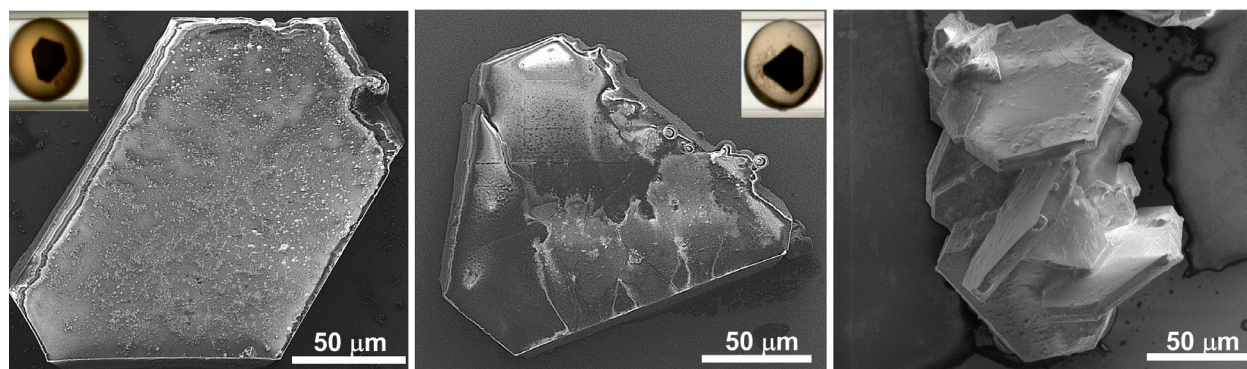
**Figure S3.** Low resolution and high resolution SEM images of colloidal crystals grown from 20 nm  $\text{CoFe}_2\text{O}_4$  NCs using ethanol (a,b) and isopropanol (c,d) as precipitants (nonsolvents). Insets show optical images of the plugs with colloidal crystals nucleated at the interface (insert in panel a) and in the bulk of solution (insert in panel b).



**Figure S4.** SEM images of colloidal crystals grown from: (a) 10 nm PbS NCs, (b) 7 nm Au NCs, (c) 11 nm  $\text{CoFe}_2\text{O}_4$  NCs and (d) 3 nm PbS NCs.

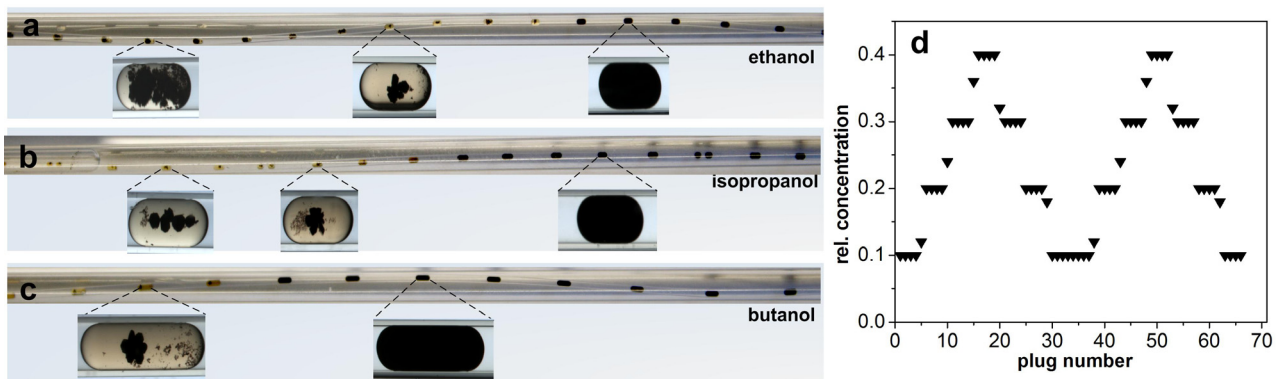


**Figure S5.** High-resolution SEM images of the surfaces of colloidal crystals grown from 20 nm  $\text{CoFe}_2\text{O}_4$  NCs showing well resolved (a) terraces, kinks, vacancies, and ledges and (b) screw dislocation.

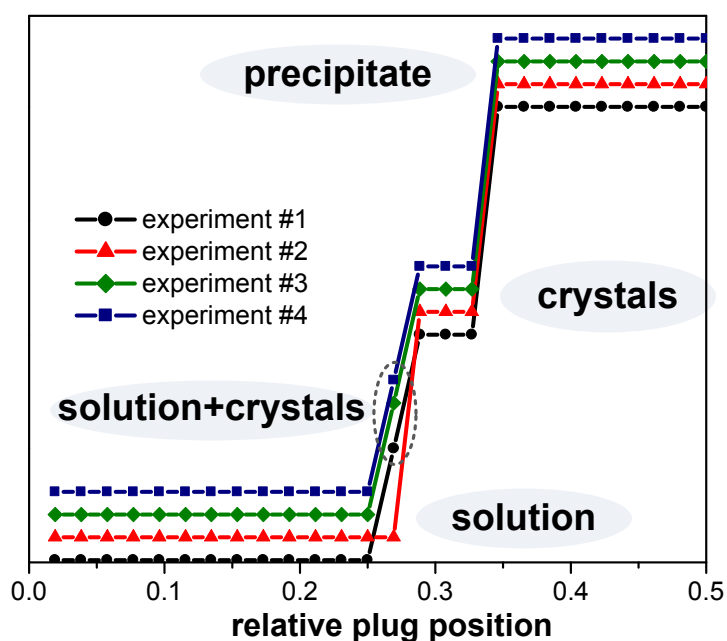


**Figure S6.** SEM images of  $\text{CoFe}_2\text{O}_4$  NC superlattices grown in the microfluidic plugs from toluene/ethanol mixtures. The insets show optical images of the plugs contained exactly same superlattices.

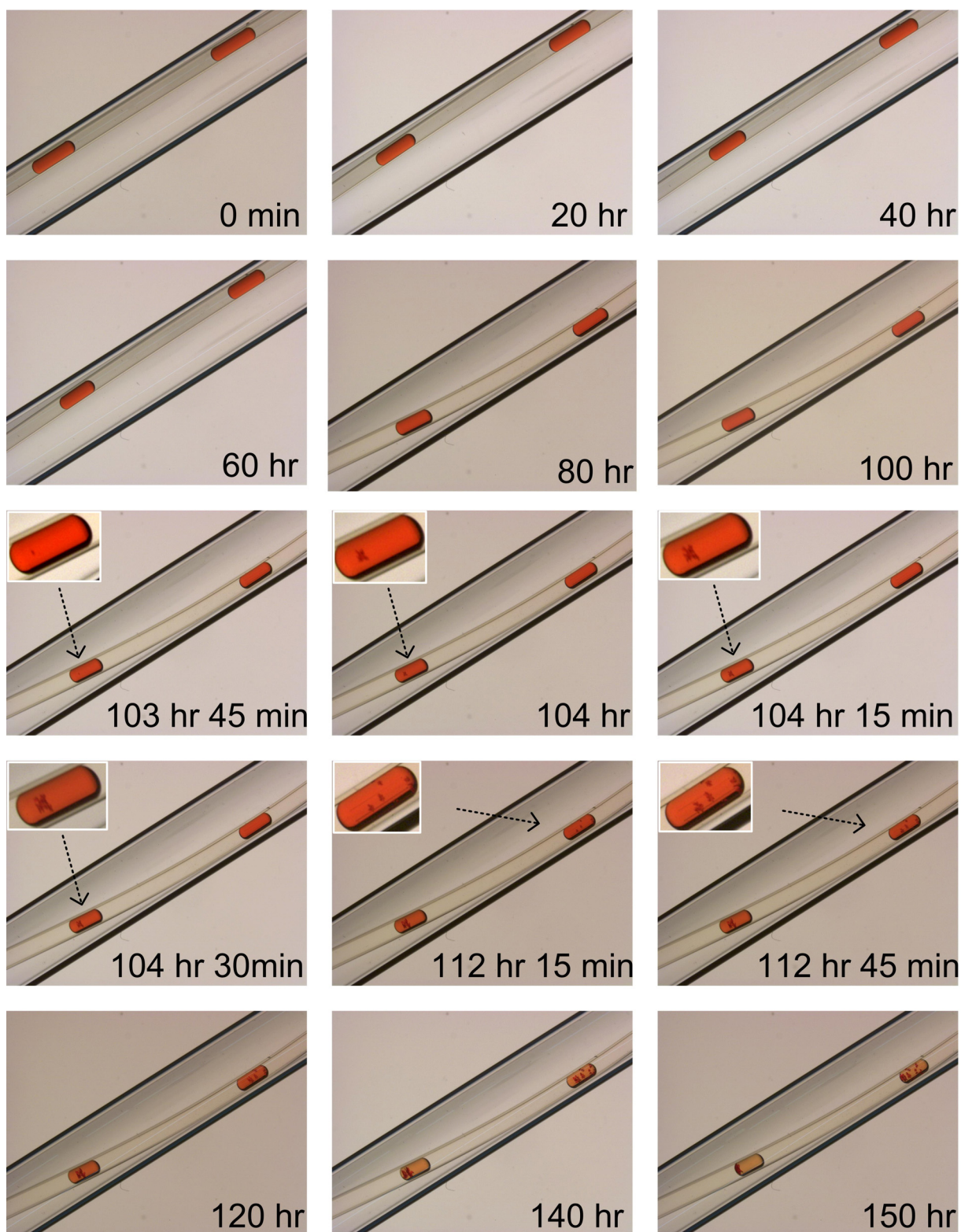




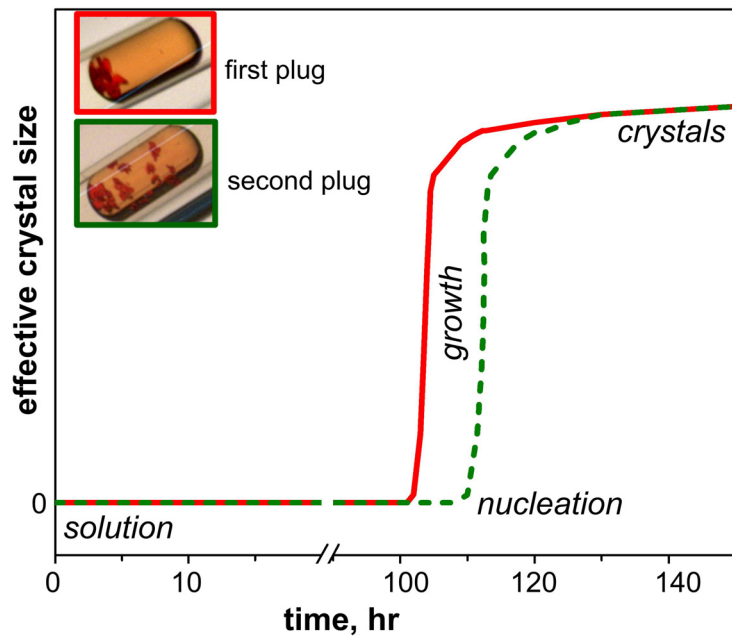
**Figure S7.** Photographs and optical images of the plugs containing 11 nm CoFe<sub>2</sub>O<sub>4</sub> NCs in toluene combined with different precipitants: (a) ethanol, (b) isopropanol, (c) n-butanol. The plugs within each capillary differ in the volume fraction of nonsolvent (10-40%). Decreasing non-solvent concentration led to the transitions from precipitate to clear solutions through the crystal formation. The solvent-to-precipitant ratio was controlled by a computer program according to plot shown in (d).



**Figure S8.** “Phase diagrams” for self-assembly of 11 nm CoFe<sub>2</sub>O<sub>4</sub> NCs in microfluidic plugs observed in four identical experiments where n-butanol concentration was varied from 10 to 80 volume percent. The curves corresponding different runs were vertically shifted for clarity. The incubation time was 4 days.

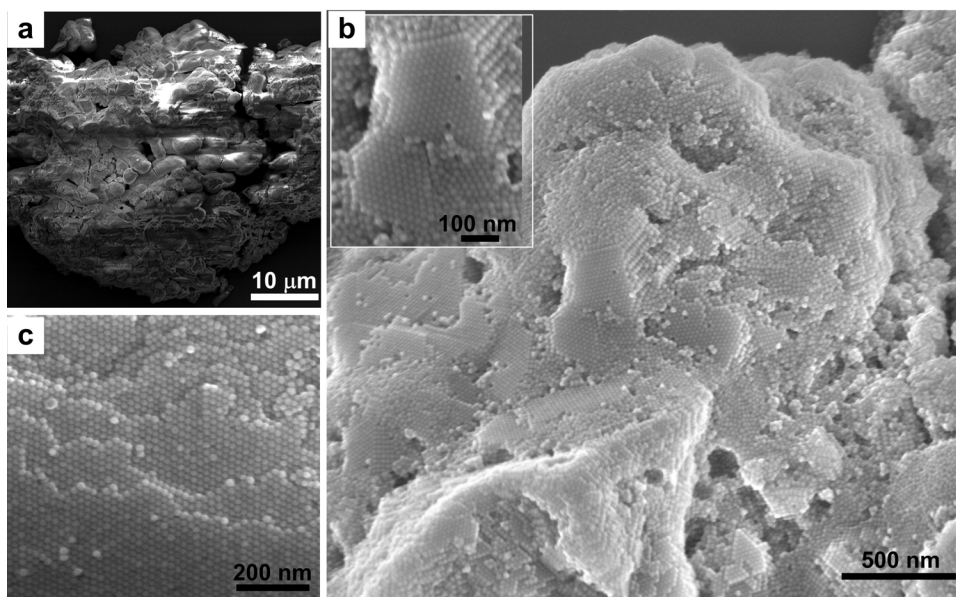


**Figure S9.** Real time monitoring of self-assembly of CdSe NCs from the toluene/ethanol mixture. The plugs with elongated shape were prepared to prevent plugs movement during experiment. To achieve this, we used a capillary with 600  $\mu\text{m}$  diameter and prepared spherical plugs which were transferred into a smaller 400  $\mu\text{m}$  diameter tube where the plugs were compressed into elongated shapes. The digital camera was set to take an image every 15 min.

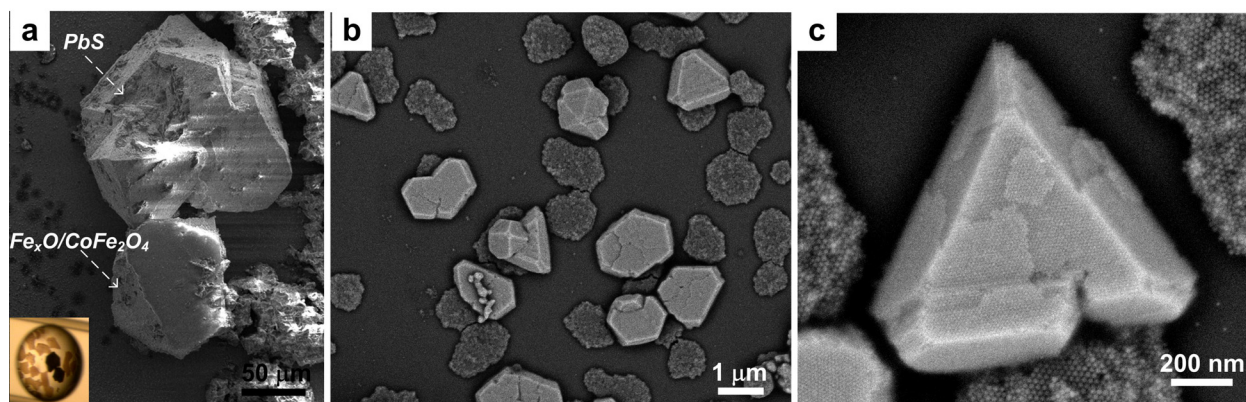


**Figure S10.** The kinetic study of nucleation and growth of 3 nm CdSe NC superlattices in two microfluidic plug containing toluene and ethanol as solvent and precipitant, respectively.

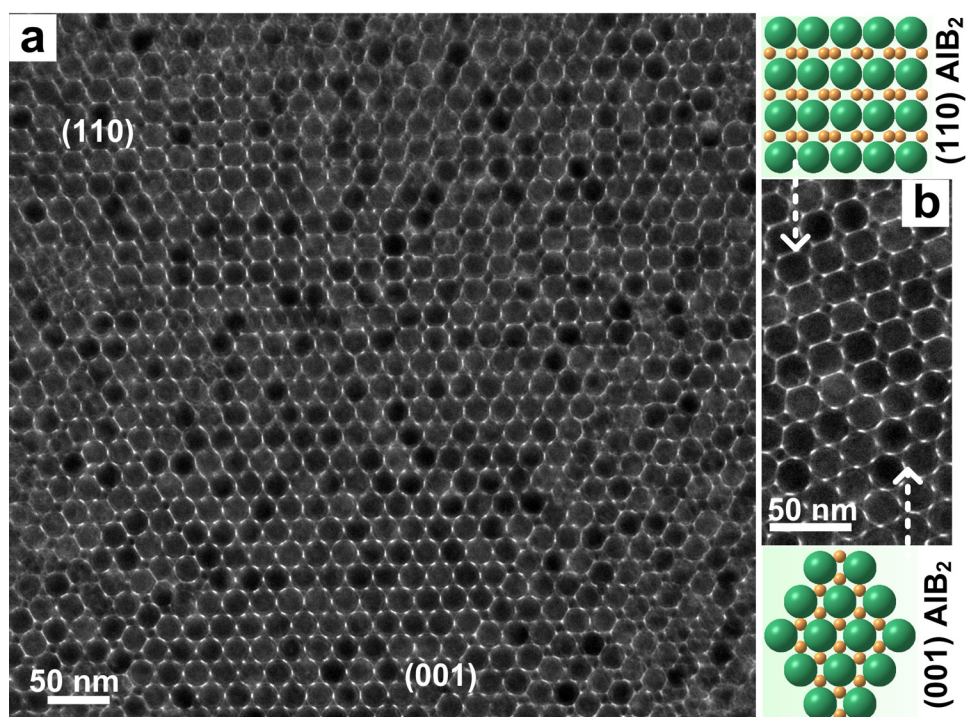




**Figure S11.** (a) Low resolution SEM image of precipitate from 20 nm  $\text{CoFe}_2\text{O}_4$  NCs obtained by plug evaporation; (b, c) high resolution SEM images of the precipitate shows long range ordering of 22 nm  $\text{CoFe}_2\text{O}_4$  NCs.



**Figure S12.** (a, b) SEM images of phase separated colloidal crystals from the mixture of 10 nm PbS and 20 nm  $\text{CoFe}_2\text{O}_4$  NCs prepared from toluene in the presence isopropanol (insert shows a plug containing two different single component superlattices: brown one assembled from  $\text{CoFe}_2\text{O}_4$  NCs and black one assembled from PbS NCs); (c) high resolution SEM image of a superlattice of 10 nm PbS NCs.



**Figure S13.** (a) TEM image of the (001) projection of the AIB<sub>2</sub>-type BNSL self-assembled from 20 nm CoFe<sub>2</sub>O<sub>4</sub> NCs and 10 nm PbS NCs on a TEM grid using conventional evaporation-driven technique. (b) A grain boundary between (001) and (110) projections of AIB<sub>2</sub>-type superlattices.

### Supporting References

- (1) Hines, M. A.; Scholes, G. D. *Advanced Materials* **2003**, *15*, 1844-1849.
- (2) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001**, *1*, 207-211.
- (3) Bodnarchuk, M. I.; Kovalenko, M. V.; Groiss, H.; Resel, R.; Reissner, M.; Hesser, G.; Lechner, R. T.; Steiner, W.; Schaffler, F.; Heiss, W. *Small* **2009**, *5*, 2247-2252.
- (4) Zheng, N.; Fan, J.; Stucky, G. D. *J. Am. Chem. Soc.* **2006**, *128*, 6550-6551.
- (5) Shevchenko, E. V., Talapin, D. V., Murray, C. B., O'Brien, S. *J. Am. Chem. Soc.* **2006**, *128*, 3620-3637.
- (6) Tice, J. D.; Song, H.; Lyon, A. D.; Ismagilov, R. F. *Langmuir* **2003**, *19*, 9127-9133.
- (7) Roach, L. S.; Song, H.; Ismagilov, R. F. *Anal. Chem.* **2005**, *77*, 785-796.
- (8) Li, L.; Mustafi, D.; Fu, Q.; Tereshko, V.; Chen, D. L. L.; Tice, J. D.; Ismagilov, R. F. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 19243-19248.
- (9) Pompano, R. R.; Li, H. W.; Ismagilov, R. F. *Biophysical Journal* **2008**, *95*, 1531-1543.