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Supplementary Information for

Controllable Synthesis of Star-shaped $FeCoMnO_x$ Nanocrystals and Their Self-Assembly into Superlattices with Low-Packing Densities

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Experimental Section

Materials

Chlorate hydrates of transition metals ($FeCl_3 \cdot 6H_2O$, 99.9%, $CoCl_3 \cdot 6H_2O$, and $MnCl_2 \cdot 6H_2O$), 1-octadecene (ODE, 90%), and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Sodium oleate (NaOA) was purchased from Tokyo Chemical Industry Co. Ltd.

Preparation of the mixed-metal oleate precursors

The mixed-metal oleate precursors were synthesized by the reaction of metal chlorides with sodium oleate.[1] In a typical synthesis, $FeCl_3 \cdot 6H_2O$ (10 mmol), $MnCl_2 \cdot 4H_2O$ (10 mmol), $CoCl_3 \cdot 6H_2O$ (10 mmol), and NaOA (80 mmol) were mixed with 140 mL of hexane, 80 mL of ethanol, and 60 mL of H_2O in a 500 mL round-bottom flask. The flask was refluxed at 70 ℃ for 5 h in an oil bath. After cooling to room temperature, the mixture was then transferred to a separatory funnel and washed thoroughly, at least five times, with deionized water to remove any impurities and excess reactants. The upper organic phase, containing the metal oleate, was separated, and the subsequent removal of the solvent yields a viscous product of the mixed-metal oleate precursor.

Synthesis of colloidal star-shaped $FeCoMnO_x$ NCs

The synthesis of star-shaped $FeCoMnO_x$ NCs, capped with OA ligands, involves the use of the mixed-metal oleate precursors prepared earlier.[2] In a 100-mL three-neck flask, 4.5 g of the previously prepared metal oleate was combined with 1.5 g of OA and 1.5 g of NaOA in 20 g of ODE. The mixture was heated to 50 °C and the flask was evacuated three times and refilled with N_2. The reaction solution was then heated to 120 °C and again evacuated three times in the same manner and kept under vacuum for 2 h. The system was then heated under N_2 to 315 °C and maintained at this temperature for 3 h. After cooling to room temperature, the product was divided equally into three centrifuge tubes with 20 ml of isopropanol and 5 ml of ethanol added to each tube and then centrifuged for 5 min at 5000 rpm. The resultant pellets were redispersed in 20 mL

of hexane, and the washing process was repeated to purify the NCs. The final precipitate was dispersed in 10 mL of hexane to form a black solution with a concentration of 20 mg/mL. Reducing the decomposition time to 2 h or decreasing the amount of NaOA to 1 g resulted in the formation of cubic $FeCoMnO_x$ NCs with an edge length of 20 nm instead of star-shaped NCs.

Self-assembly of 2D superlattices

In a typical procedure, a hexane solution containing star-shaped $FeCoMnO_x$ NCs was prepared.[3] This NC solution was carefully drop-casted onto the surface of DEG in a Teflon well, which was then covered with a glass slide. As hexane slowly evaporated, a solid membrane of 2D superlattices formed, which could be transferred from the DEG surface to other substrates for further characterization. 2D superlattices with various structures can be obtained by varying the NC building blocks under otherwise similar conditions.

Characterization

Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM) images, and energy dispersive X-ray spectroscopy (EDS) were recorded on a Tecnai G2 F20 S-Twin microscope operated at 200 kV. Scanning electron microscope (SEM) and high-resolution SEM (HRSEM) images were obtained using a Zeiss Gemini SEM500 field emission microscope operated at 3 kV. Synchrotron beam line16B, Shanghai Synchrotron Radiation Light Source. The wavelength of an X-ray is 0.124 nm, and the scattering patterns were collected with a Pilatus 2M detector (Dectris, Switzerland). The distance between the sample and detector was 2138 mm, and the exposure time was 60 s.

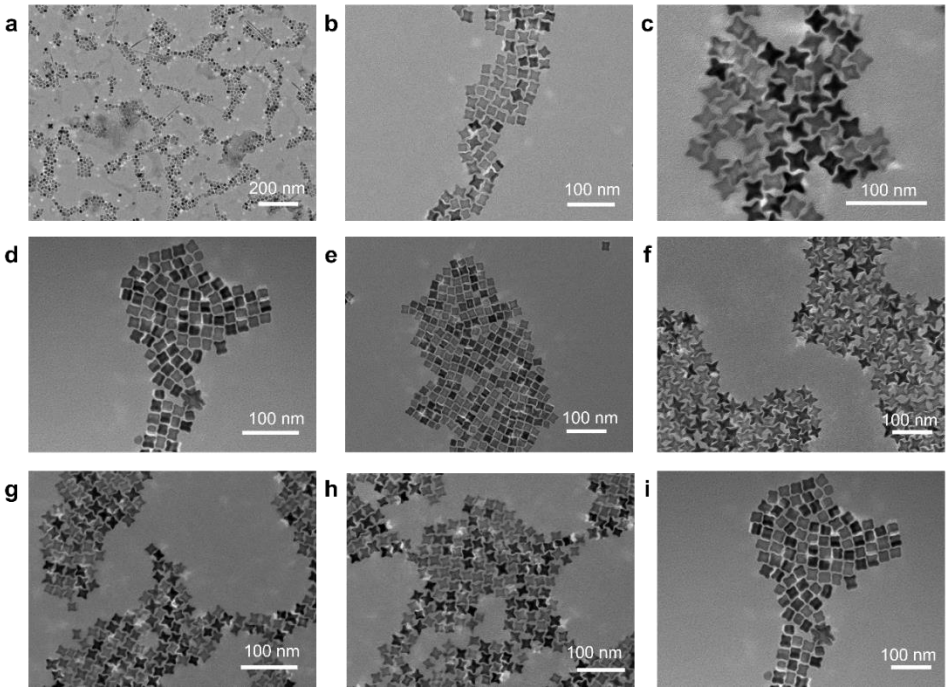


Figure S1. TEM images of $FeCoMnO_x$ NCs synthesized at different mass ratios between NaOA and the metal oleate precursor: (a) 0.1, (b) 0.3, and (c) 0.5, when performing the reactions at 315 °C over a duration of 4 h. TEM images of $FeCoMnO_x$ NCs synthesized over different reaction durations: (d) 2 h, (e) 3 h, and (f) 4 h, when performing the reactions at 315 °C with a constant NaOA to metal oleate ratio of 0.5. TEM images of $FeCoMnO_x$ NCs obtained at various temperatures: (g) 310 °C, (h) 315 °C, and (i) 325 °C, when performing the reactions with a NaOA to metal oleate ratio of 0.5 for a fixed duration of 4 h.

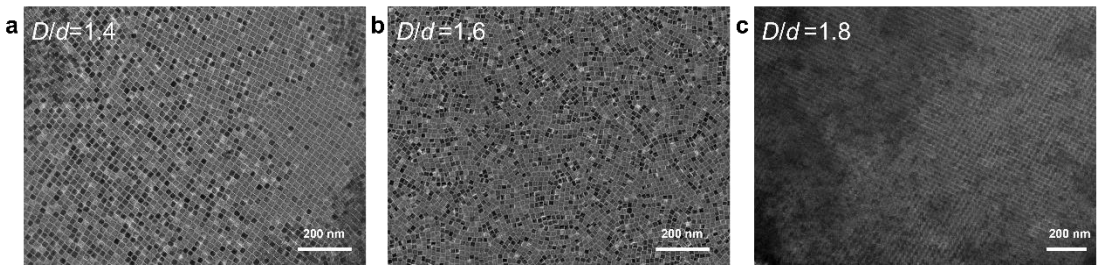


Figure S2. (a-c) Additional low-magnification TEM images of 2D superlattices self-assembled from $FeCoMnO_x$ NCs with different *D*/*d* ratios.

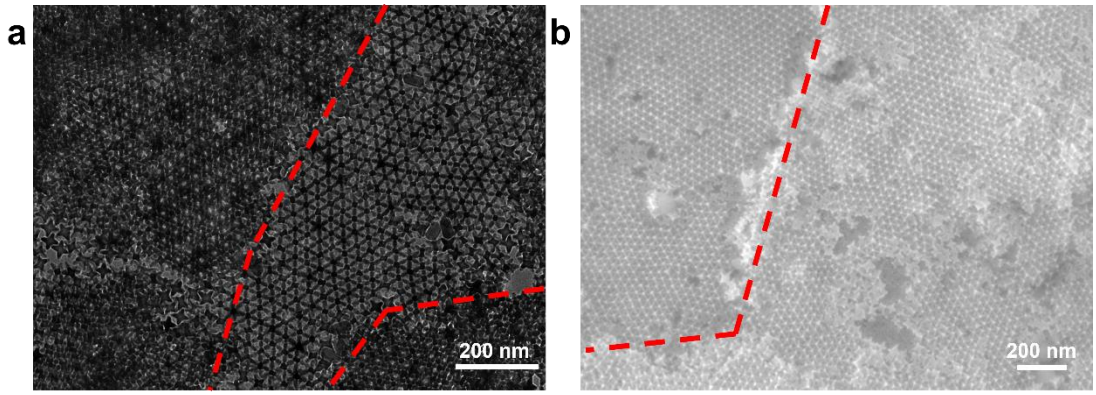
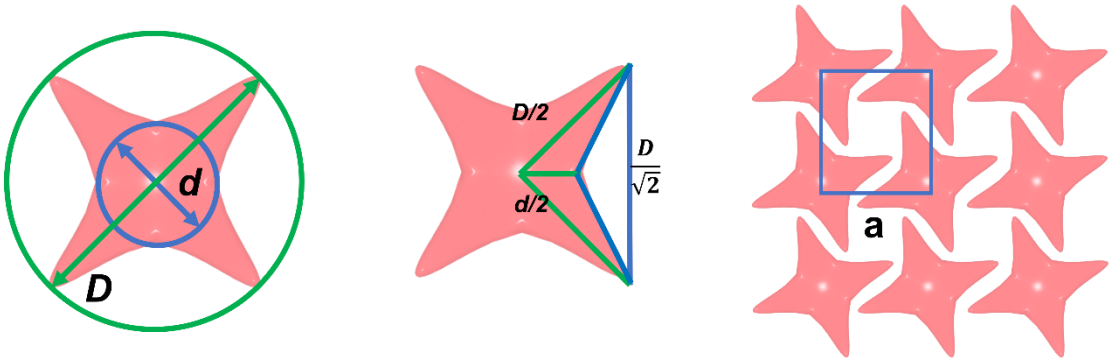


Figure S3. Additional (a) TEM and (b) SEM images of *p6m*-type superlattices, showing the grain boundaries (indicated by the dashed lines) between the monolayer and bilayer superlattices.

Note 1. Calculation of the 2D packing density of single-component superlattices comprising $FeCoMnO_x$ stars by treating each star as a cross-shaped object.

Based on the schemes shown below, the area of the blue triangle ($S_{\text{blue triangle}}$) can be calculated using the equation:

$$S_{blue\ triangle} = \frac{D}{2\sqrt{2}}\left(\frac{D}{2\sqrt{2}} - \frac{d}{2}\right)$$



The area of a single star (S_{star}) can be calculated using the equation:

$$S_{star} = S_{square} - 4S_{blue\ triangle} = \frac{Dd}{2\sqrt{2}}$$

Therefore, the packing density (ρ) of the 2D star superlattices is calculated as follows[4]:

$$\rho = \frac{S_{star}}{S_{sublattice}} = \frac{Dd}{\sqrt{2}a^2} \approx 0.61$$

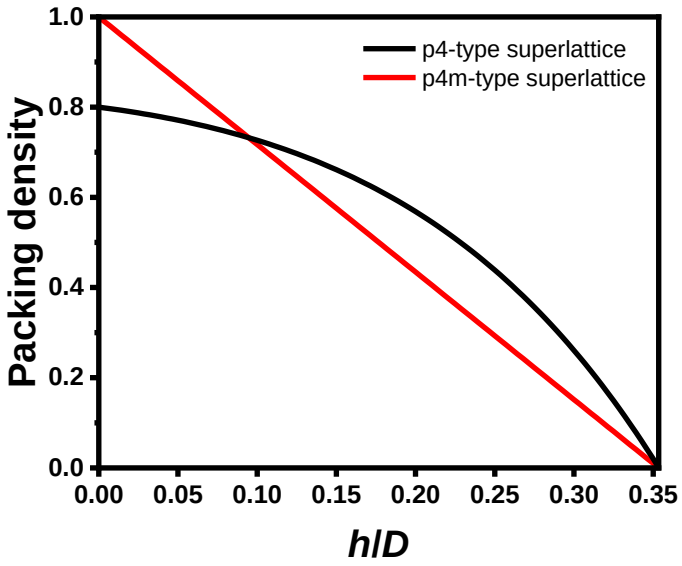
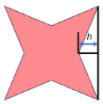


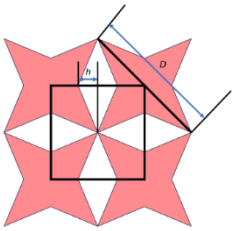
Figure S4. Space-filling curves of *p*4*m*- and *p*4-type of superlattices, respectively.

Calculation of the 2D packing density of p4m-type superlattices

Based on the schemes shown below, the projected area of star-shaped NCs can be calculated using the equation:

$$S_{star} = \frac{D^2}{2} - \sqrt{2}Dh$$



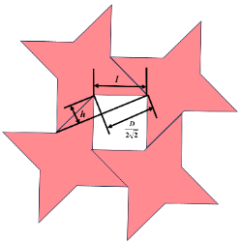


Therefore, the packing density (ρ) of the *p*4*m*-type superlattices is calculated as follows:

$$\rho = \frac{S_{star}}{S_{unitcell}} = 1 - \frac{2\sqrt{2}h}{D}$$

Calculation of the 2D packing density of p4-type superlattices

Based on the scheme shown below, the area of voids in *p*4-type superlattices can be calculated by:



$$S_{void} = \frac{D^2}{8} + h^2$$

Therefore, the packing density (ρ) of the *p*4-type superlattices is calculated as follows:

$$\rho = \frac{S_{star}}{S_{star} + S_{void}} = \frac{1 - 2\sqrt{2}\frac{h}{D}}{1.25D^2 - 2\sqrt{2}\frac{h}{D} + 2(\frac{h}{D})^2}$$

Reference

1. J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang and T. Hyeon, *Nat. Mater.*, 2004, **3**, 891-895.
2. J. Kim, W. Ko, J. M. Yoo, V. K. Paidi, H. Y. Jang, M. Shepit, J. Lee, H. Chang, H. S. Lee, J. Jo, B. H. Kim, S. P. Cho, J. van Lierop, D. Kim, K. S. Lee, S. Back, Y. E. Sung and T. Hyeon, *Adv Mater*, 2021, **34**, 2107868.
3. A. Dong, J. Chen, P. M. Vora, J. M. Kikkawa and C. B. Murray, *Nature*, 2010, **466**, 474-477.
4. A. Dong, X. Ye, J. Chen and C. B. Murray, *Nano Lett*, 2011, **11**, 1804-1809.