

Supporting Information

Layer-by-Layer Manipulation of Anisotropic Nanoblocks : Orientation-Switched Superlattices through Orthogonal Stacking of *a* and *c* Directions

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Another types of orientation-switched superlattices (Figure S3)

Additional information

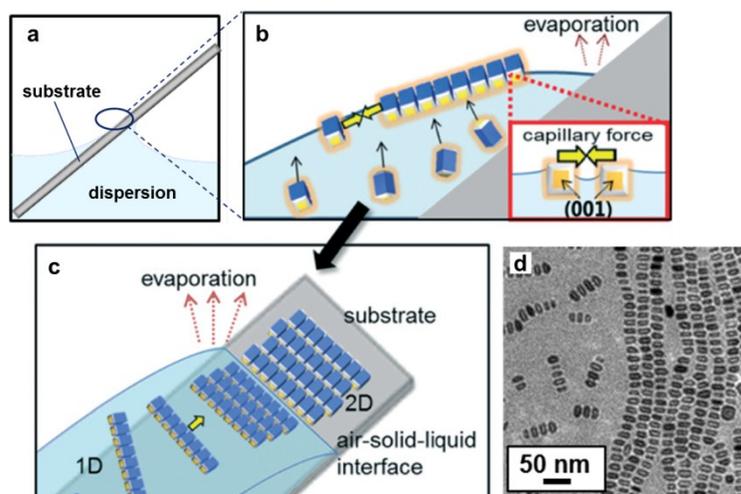


Figure S1. Schematic illustrations of the fabrication of *a*-face 2D arrays consisting of Mn_3O_4 rectangular nanoblocks through a convective self-assembly method (a-c). TEM image of the 2D arrays formed from the 1D chains (d).

a-face 2D arrays consisting of Mn_3O_4 rectangular nanoblocks were fabricated through a convective self-assembly method (Figure S1a). In previous works (ref. 2, 25), self-assembly of nanocubes and nanorods was reported to occur at the air-liquid interface. As shown in Figure S1b, the broad {100} faces of the nanocuboids located at the air-liquid interface are parallel to the interface due to their hydrophobic property. When the air-liquid interface shrinks with the evaporation of the dispersion medium, 1D chains are formed by aligning the nanocuboids facing the other {100} faces with lateral capillary force. The *a*-face 2D arrays are produced by parallel assembly of the linear chains (Figure S1c). Figure S1d shows 2D arrays formed with floating small 1D chains. This result suggests that 2D arrays are formed through assembly of linear chains by a lateral capillary force at the air-liquid-substrate interface.

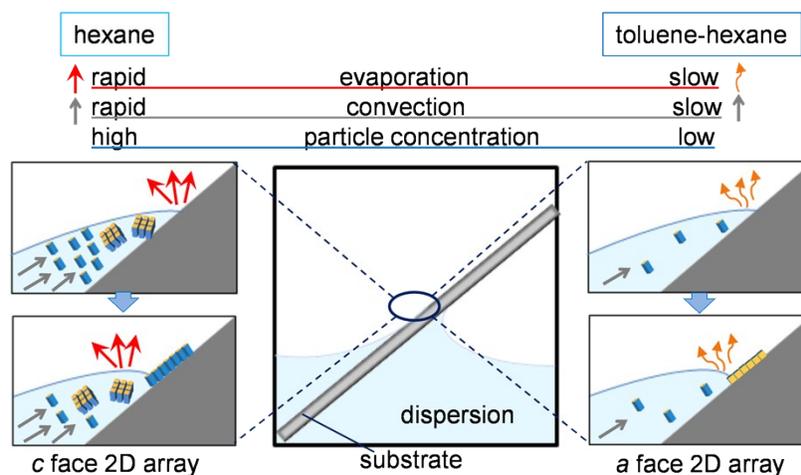


Figure S2. Schematic illustration of formation processes of *a*-face and *c*-face 2D arrays consisting of Mn_3O_4 rectangular nanoblocks through a convective self-assembly method from toluene-hexane mixture and hexane, respectively.

Because the evaporation rate of hexane is higher than that of the mixture of toluene and hexane, 2D clusters of the nanoblocks are easily formed through a rapid increase in particle concentration in the dispersion near the evaporation front. 2D clusters assemble into *c* face 2D arrays through the assembly of on a substrate after evaporation.

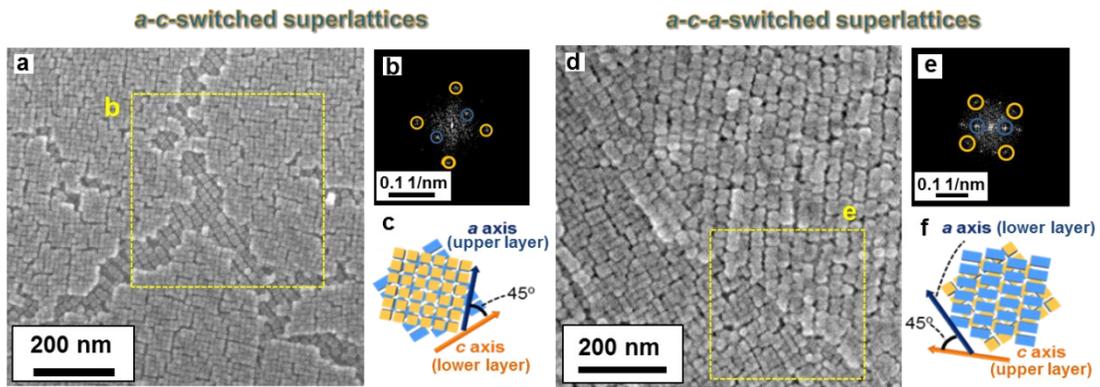


Figure S3. SEM image (a), corresponding FFT pattern (b), and schematic illustration of *a-c-switched* superlattices (c). SEM image (d), corresponding FFT pattern (e), and schematic illustration of *a-c-a-switched* superlattices (f).