Supporting Information

Spontaneous Formations of Superlattices and Supracrystals from Various Forms of Mn_3O_4 Nanocrystals

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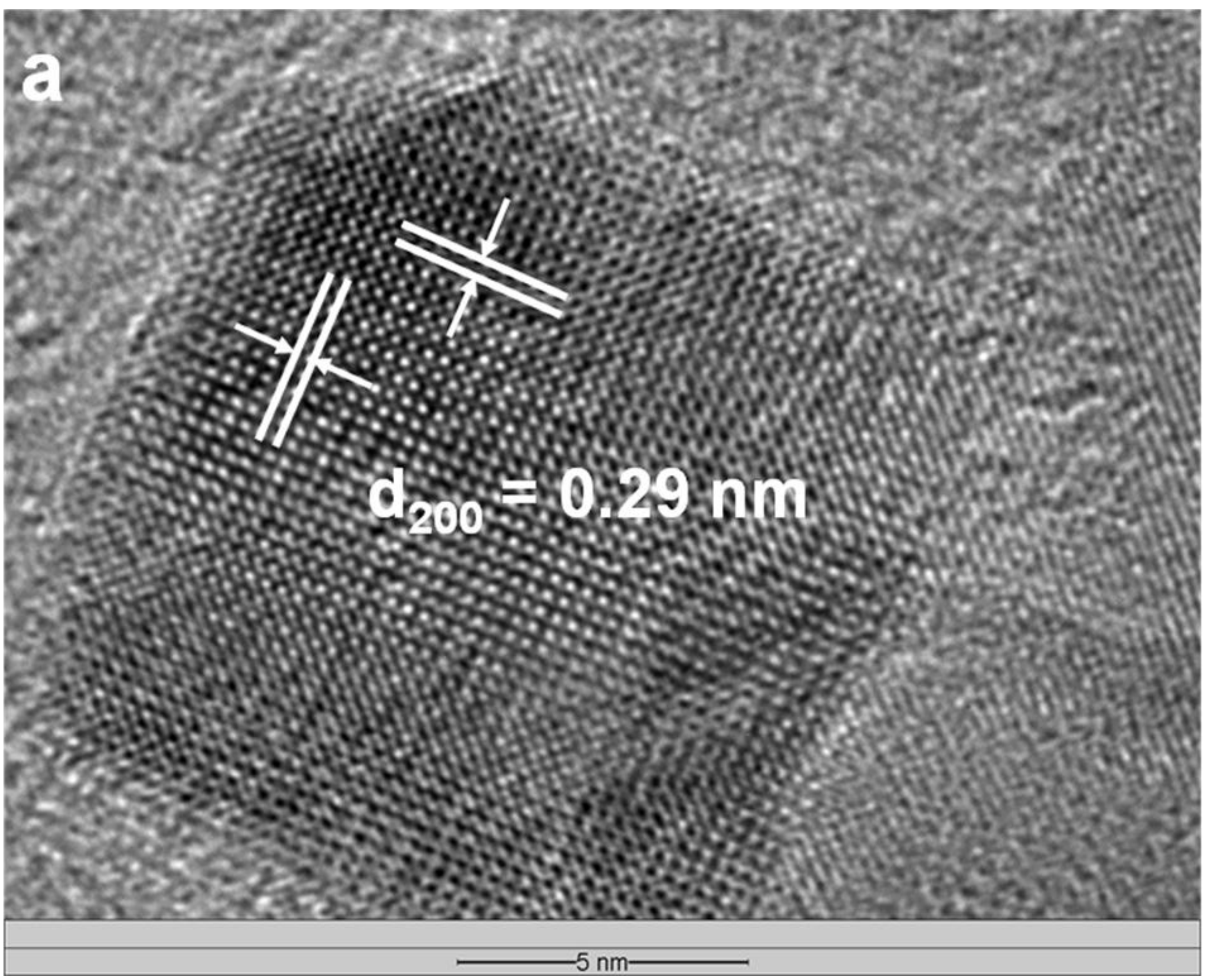
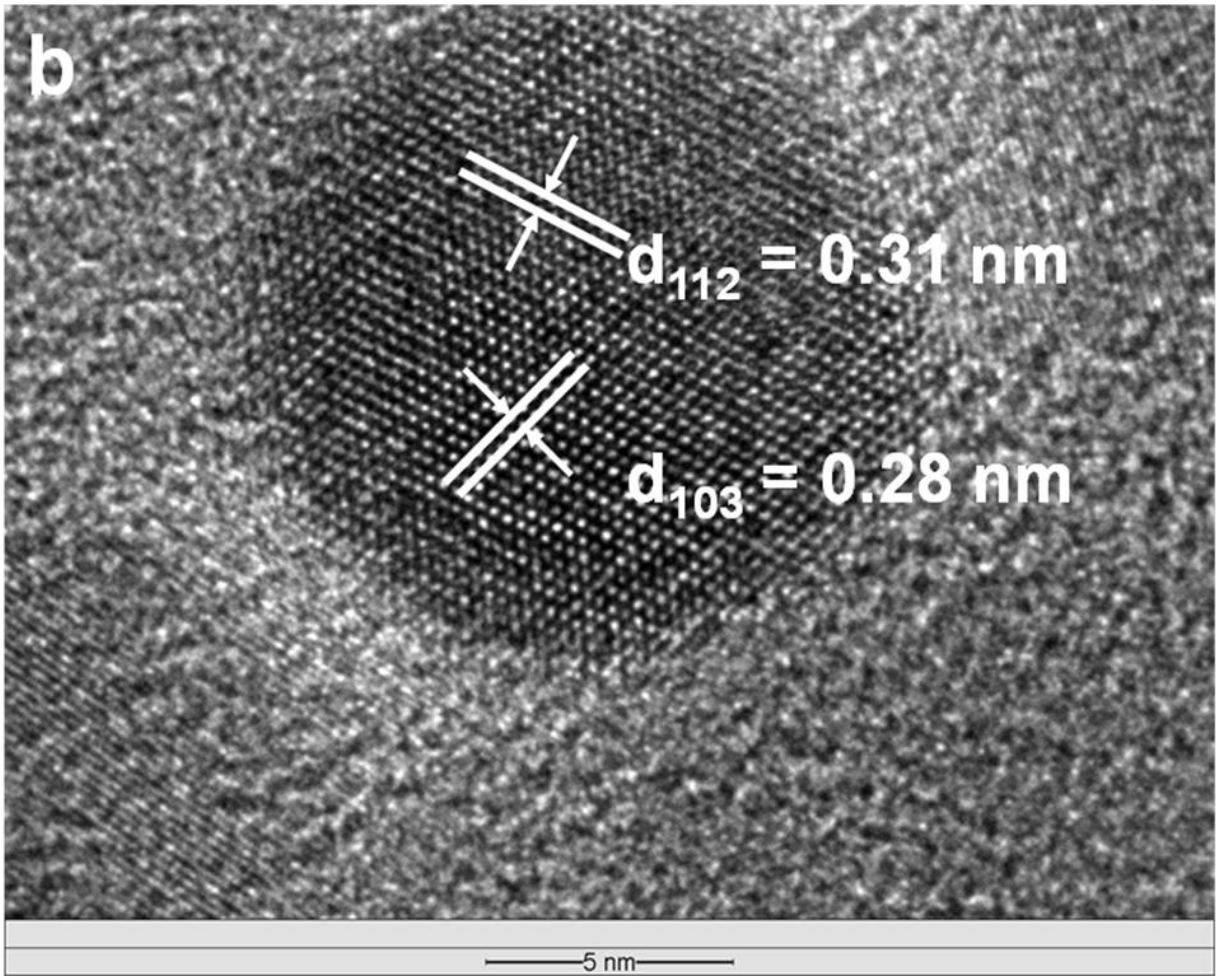
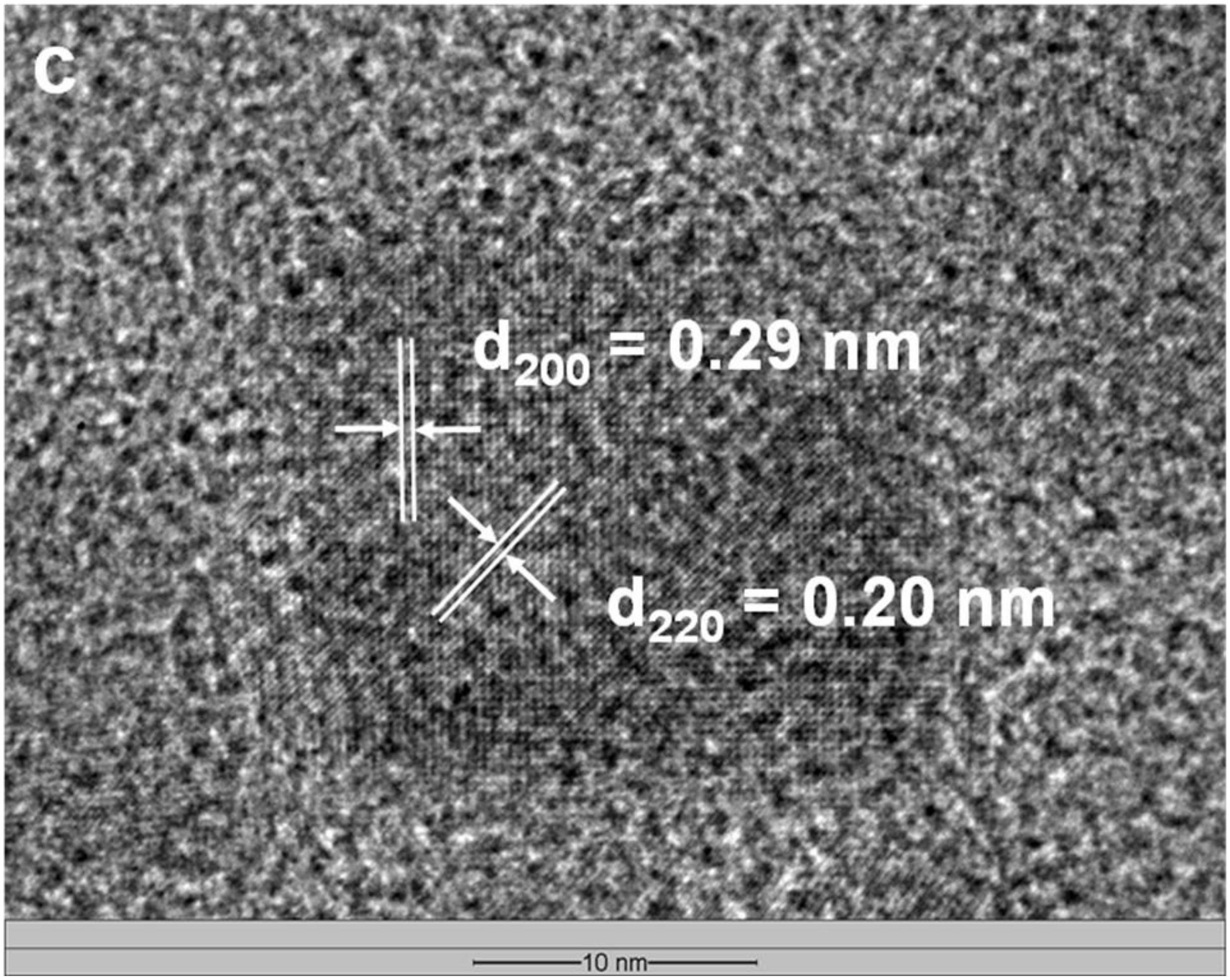
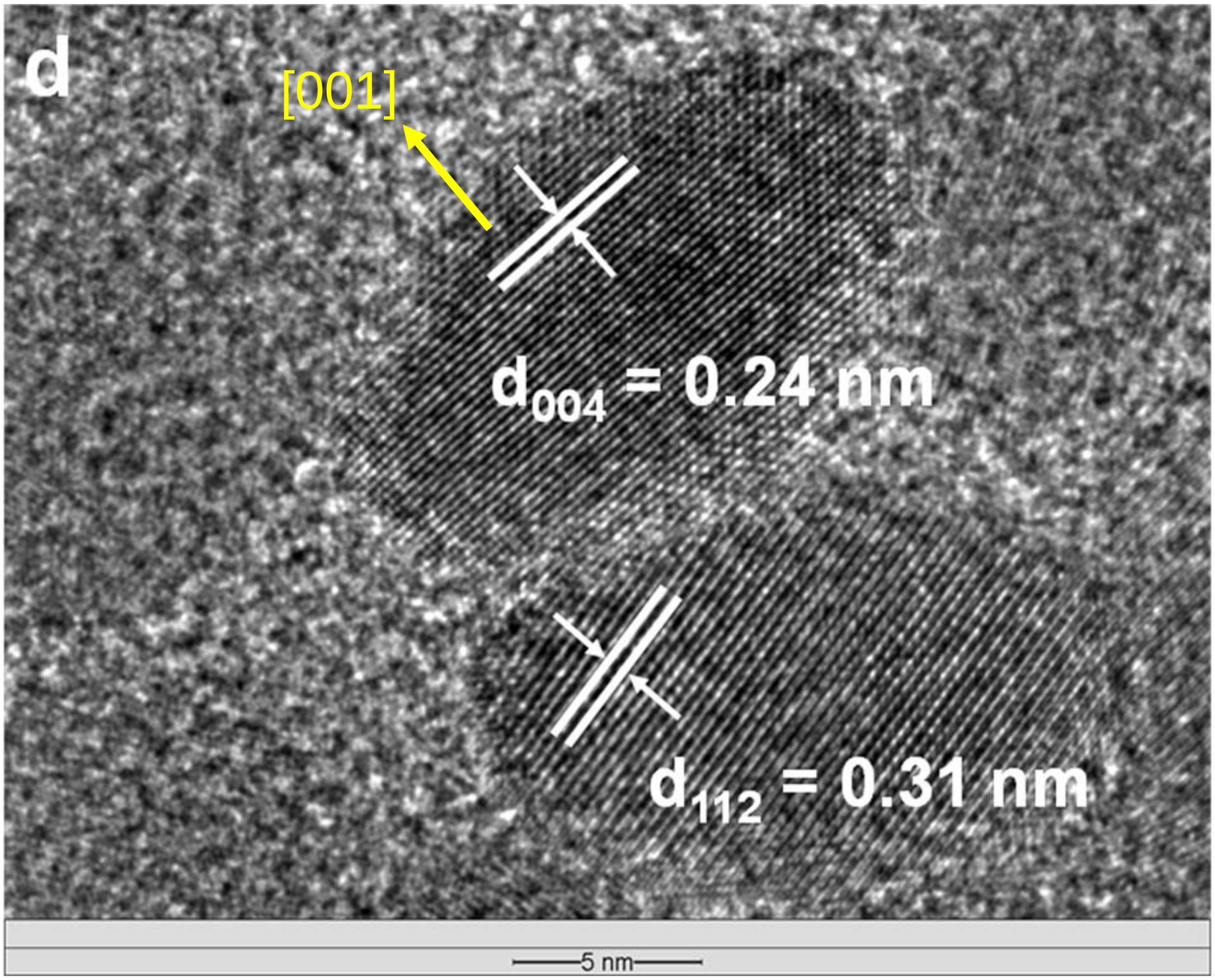
Figure S1. Analysis of HRTEM images (Figure 1e-h in the main text)



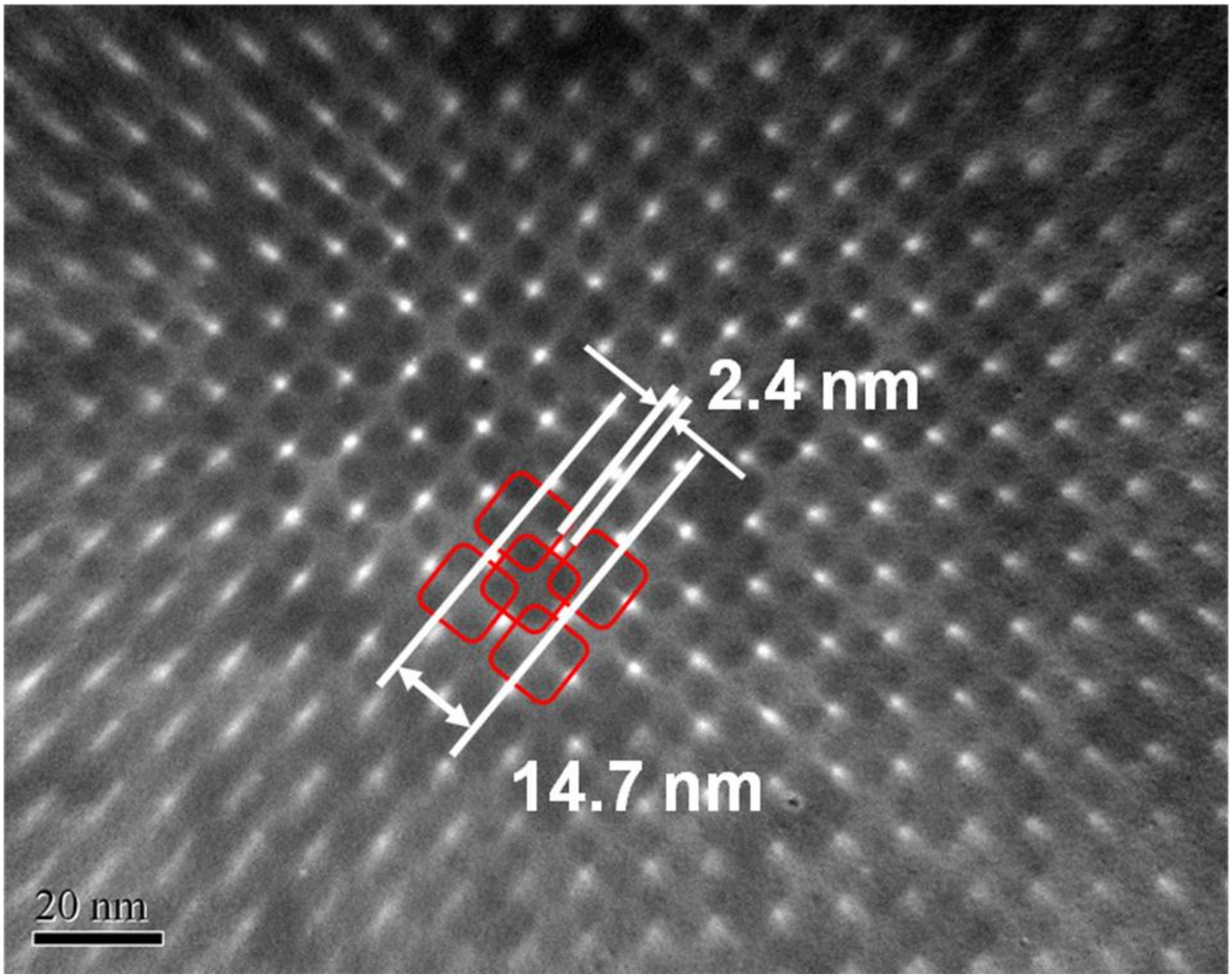

b
d112 = 0.31 nm
d103 = 0.28 nm
5 nm

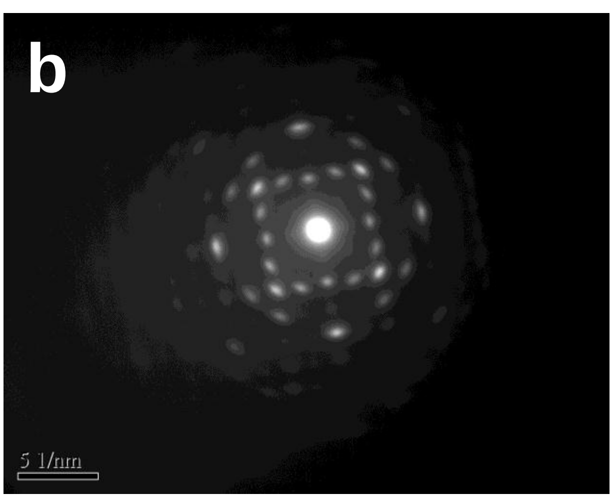

c
d_{200} = 0.29 nm
d_{220} = 0.20 nm
10 nm

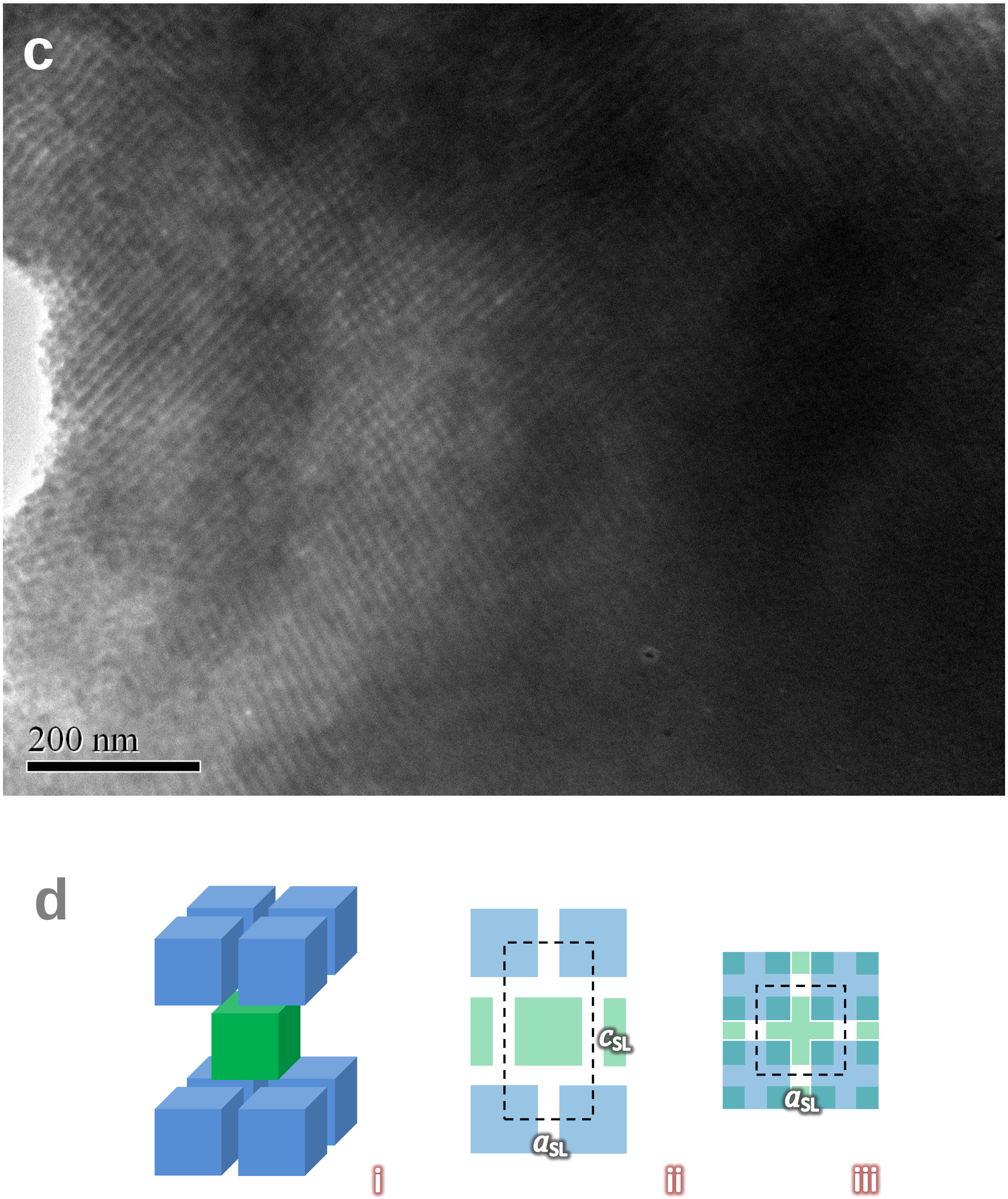


Notes: Magnified HRTEM images of the Mn_3O_4 nanocrystals reported in the main text Figure 1(e-h): (a) nanocube: the distance between marked planes is 0.29 nm, which is the *d*-spacing of (200), (b) nanosphere: the distances between the two adjacent planes are 0.28 and 0.31 nm, corresponding to *d*-spacings of (103) planes and (112) planes, respectively, (c) nanoplates: the lattice fringes are separated by 0.29 and 0.20 nm, in good agreement with the (200) and (220) lattice spacings, and (d) nanorice: the two lattice fringes are 0.24 and 0.31 nm, which are assigned to the *d*-spacings of (004) and (112) planes respectively.

Figure S2. Superlattices assembled from Mn_3O_4 nanocubes

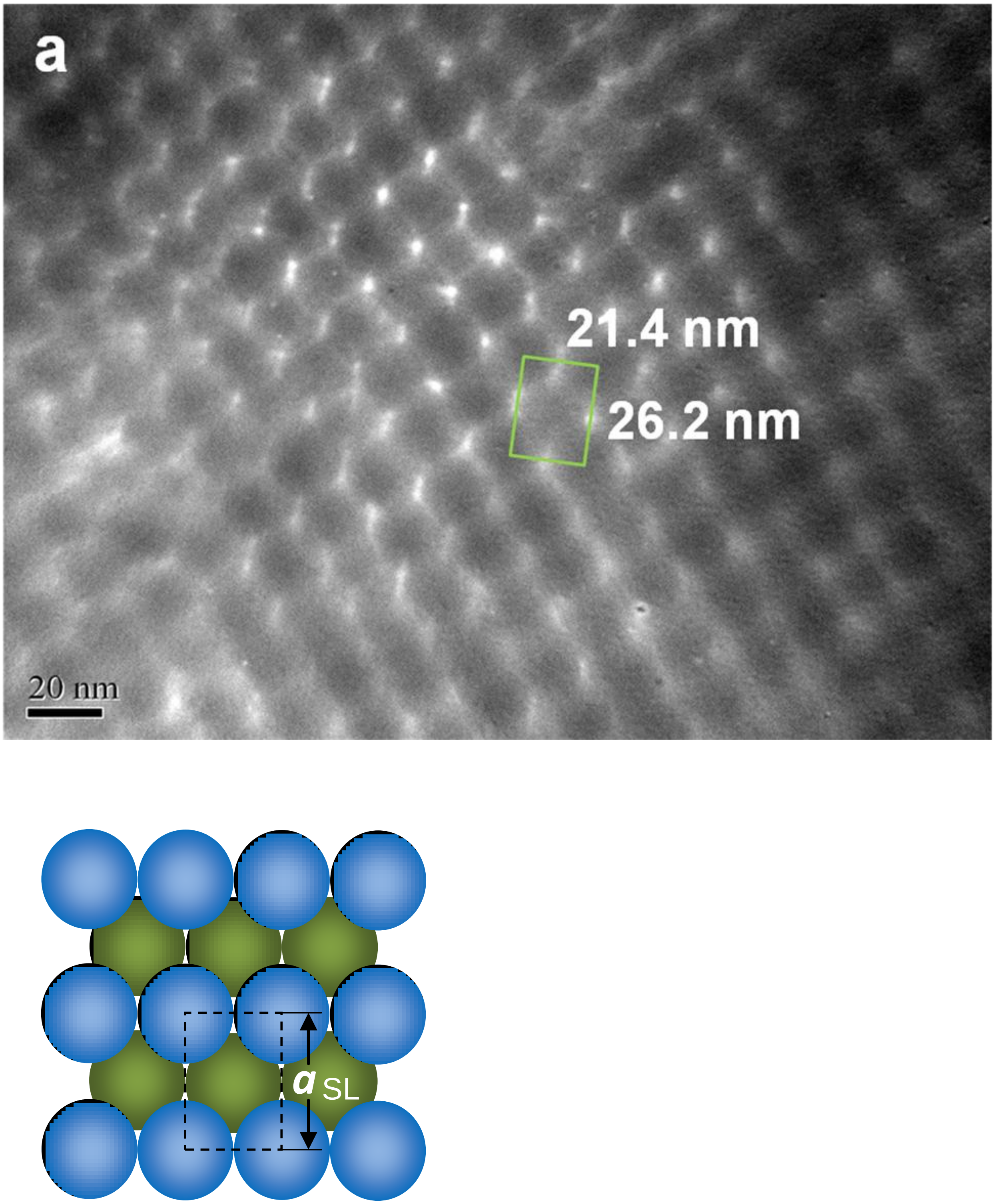


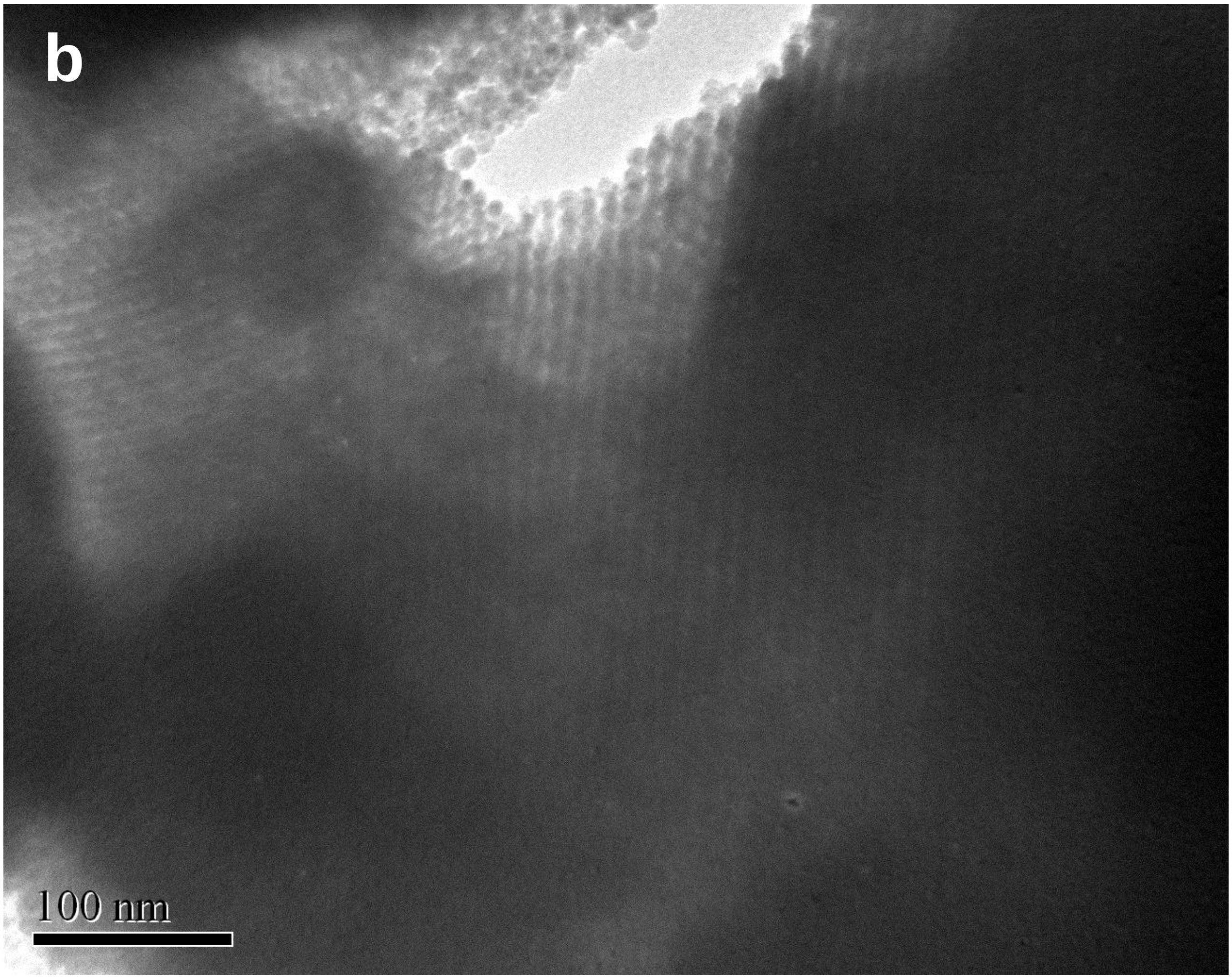




Notes: (a) Magnified TEM image (Figure 5a in the main text), (b) the electron diffraction pattern of Mn_3O_4 crystal structure (the [001] zone spots), (c) a large domain of SL formed by the Mn_3O_4 nanocubes, and (d) schematic illustrations: (i) cube stacking, (ii) side view of the unite cell, and (iii) top view of the unit cell. The average cube size in the SL is 12.3 nm. The overall crystal system for this SL is tetragonal and the lattice parameters are $a_{SL} = b_{SL} = 14.7$ nm and $c_{SL} = 29.4$ nm. Therefore, the distance between two adjacent nanocubes is 14.7 nm – 12.3 nm = 2.4 nm.

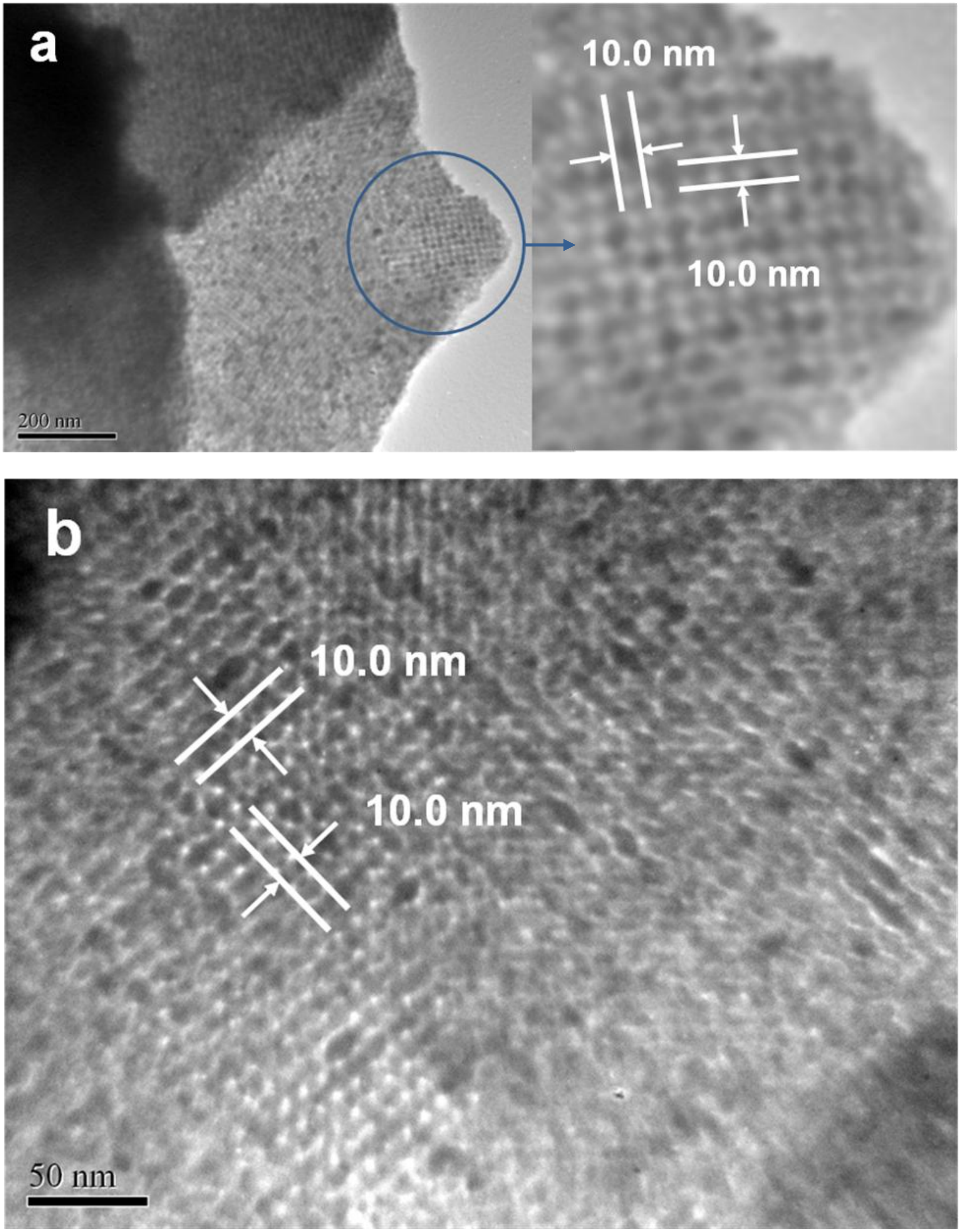
Figure S3. Superlattices assembled from Mn_3O_4 nanospheres

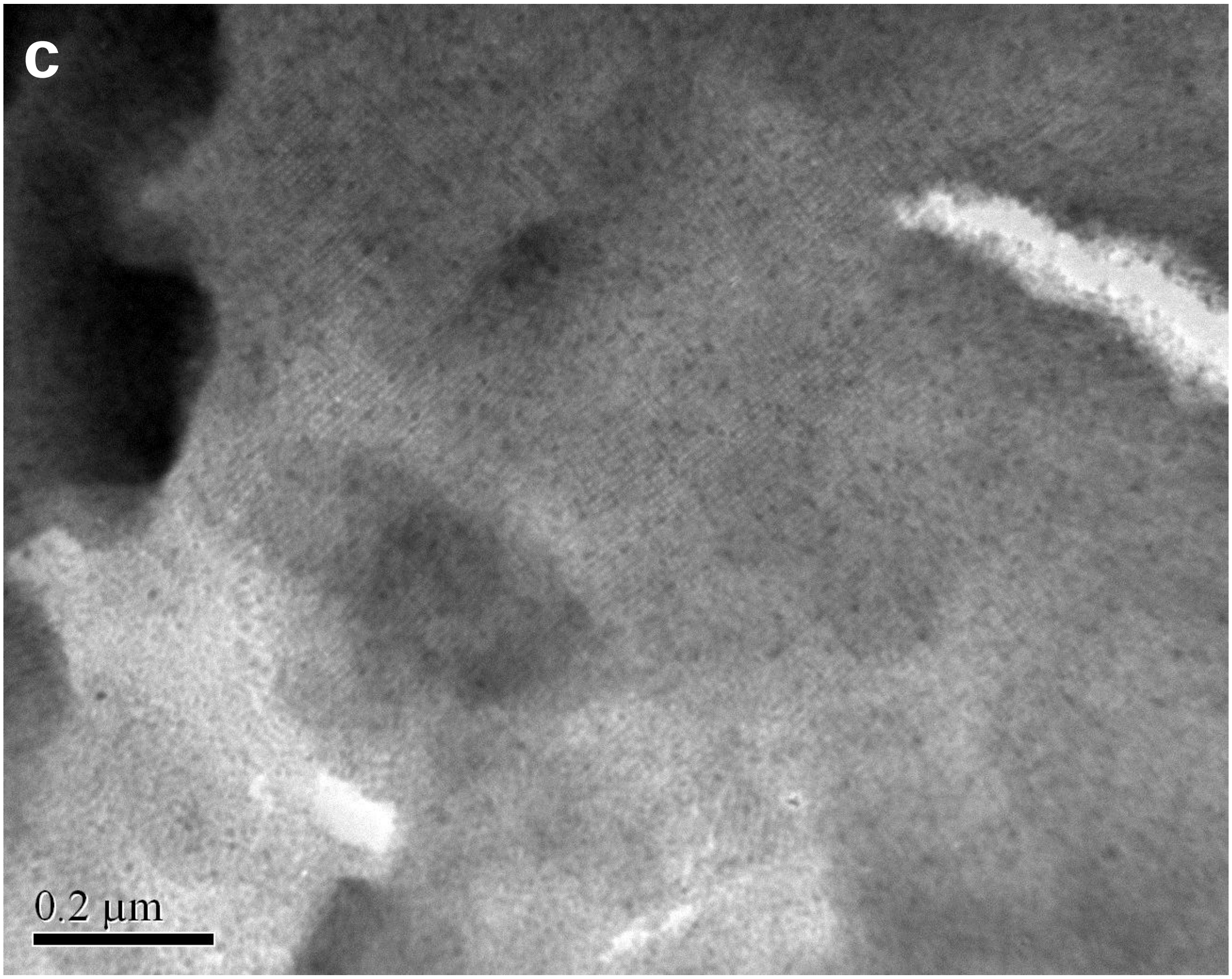




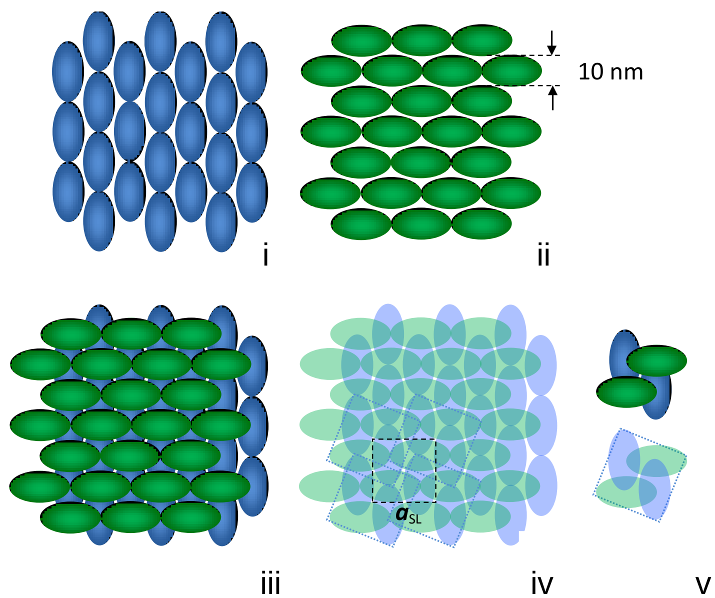
Notes: (a) Magnified TEM image (Figure 5d in the main text) with an color illustration for the $(110)_{SL}$ surface, and (b) a large domain of SL formed by nanospheres. Lattice constants of SCs (*fcc*) formed from nanospheres: $a_{SL} = 26.2$ nm (an average value). A surface unit cell is indicated in (a). However, the observed departure from the theoretical values for the surface unit cell is due to imperfect spherical structure of these nanospheres.

Figure S4. Superlattices assembled from Mn_3O_4 nanorice



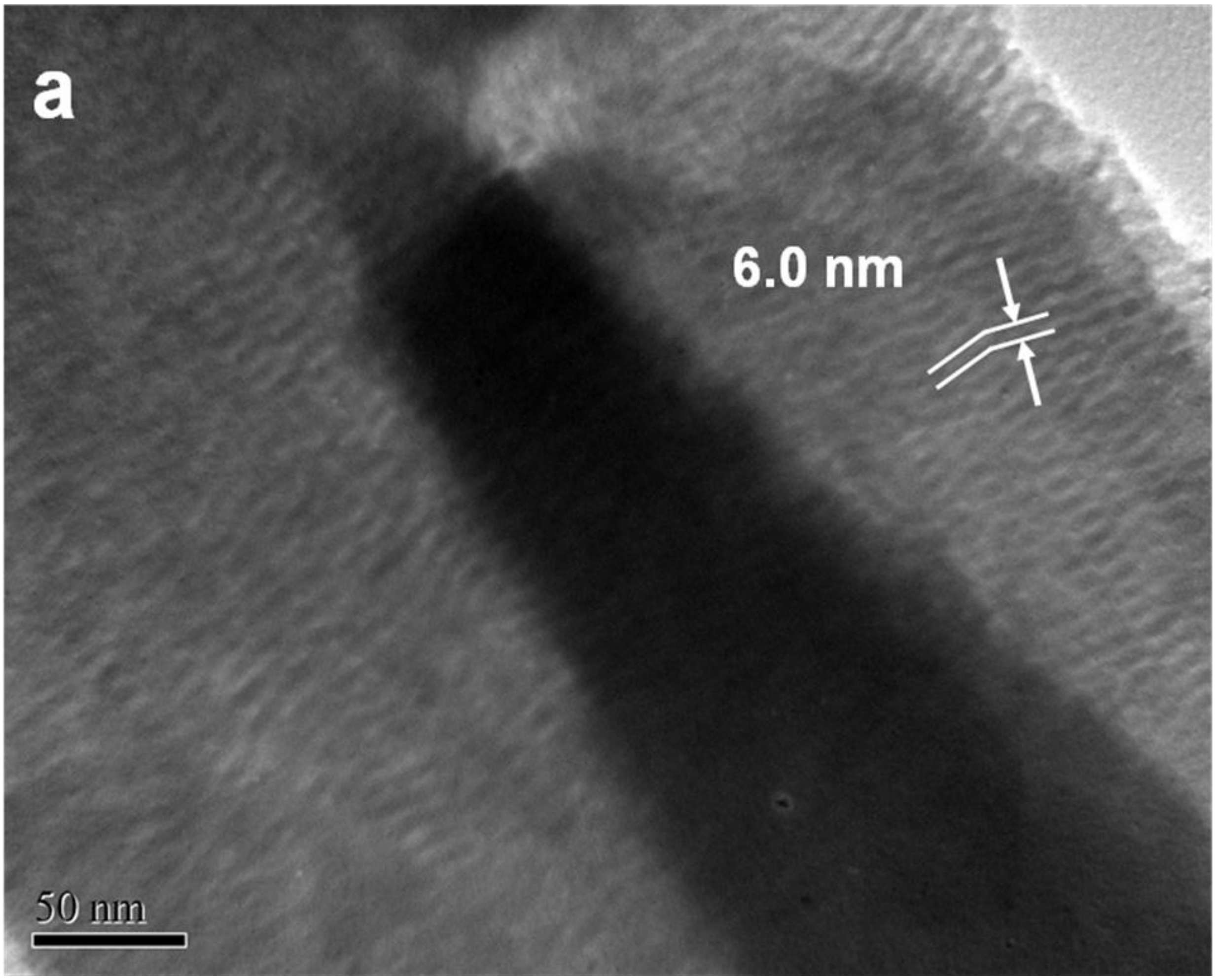

c
0.2 μm

d

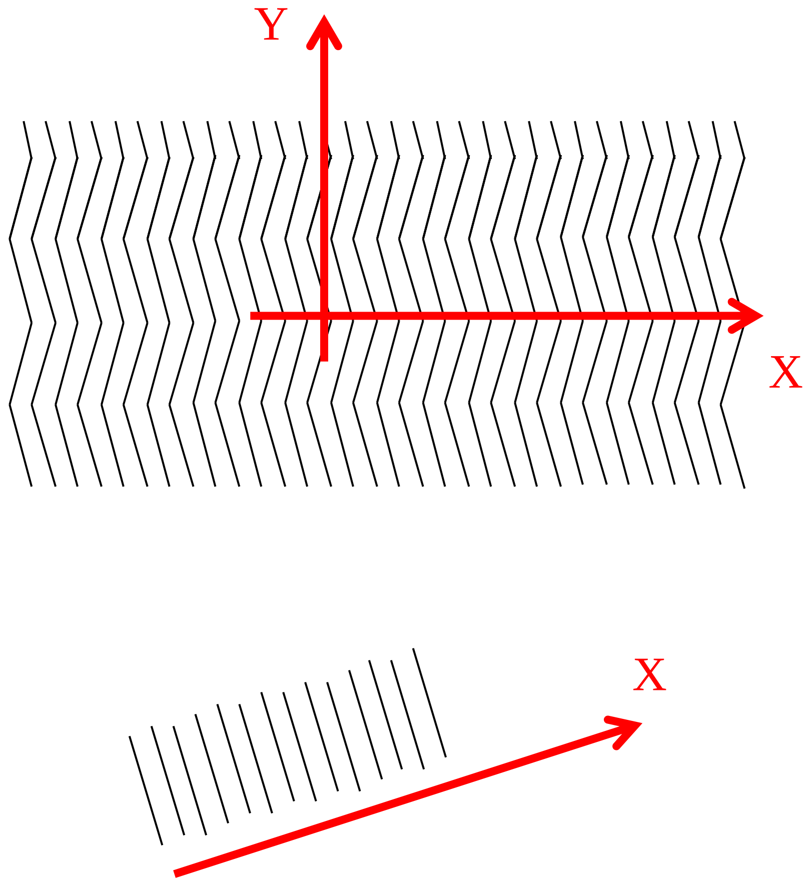


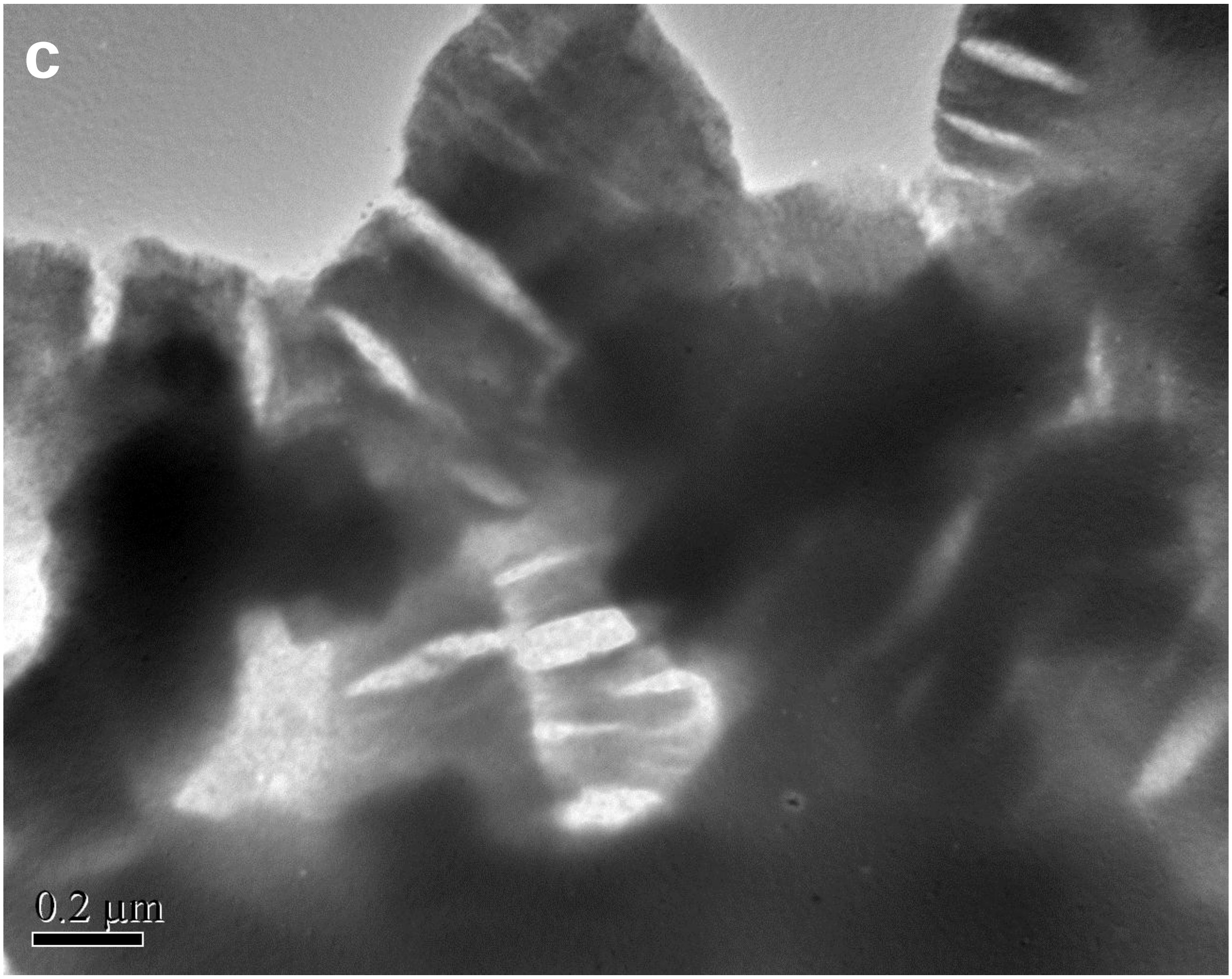
Notes: (a-b) TEM images of SLs formed from the Mn_3O_4 nanorice, (c) a large domain of SL formed by the Mn_3O_4 nanorice, and (d) Schematic illustrations of SL assembled from Mn_3O_4 nanorice: (i) the first layer of nanorice, (ii) the second layer of nanorice, (iii) a two-layer structure, (iv) transparent view of overlapping, and (v) a point unit of this crystal system. The lattice constants in this tetragonal arrangement are: $a_{SL} = b_{SL} = 20.0$ nm and $c_{SL} \approx 20.0$ nm.

Figure S5. Supracrystals assembled from Mn_3O_4 nanoplates



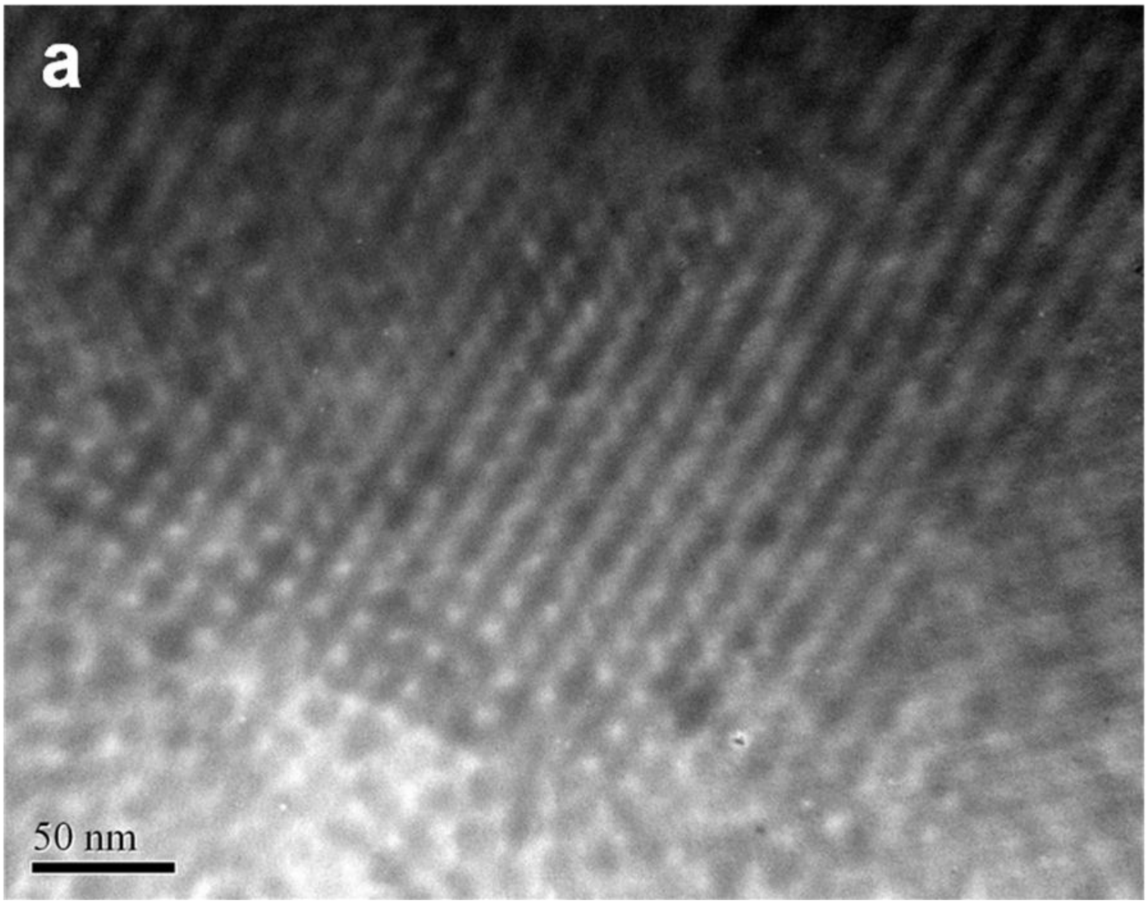
b

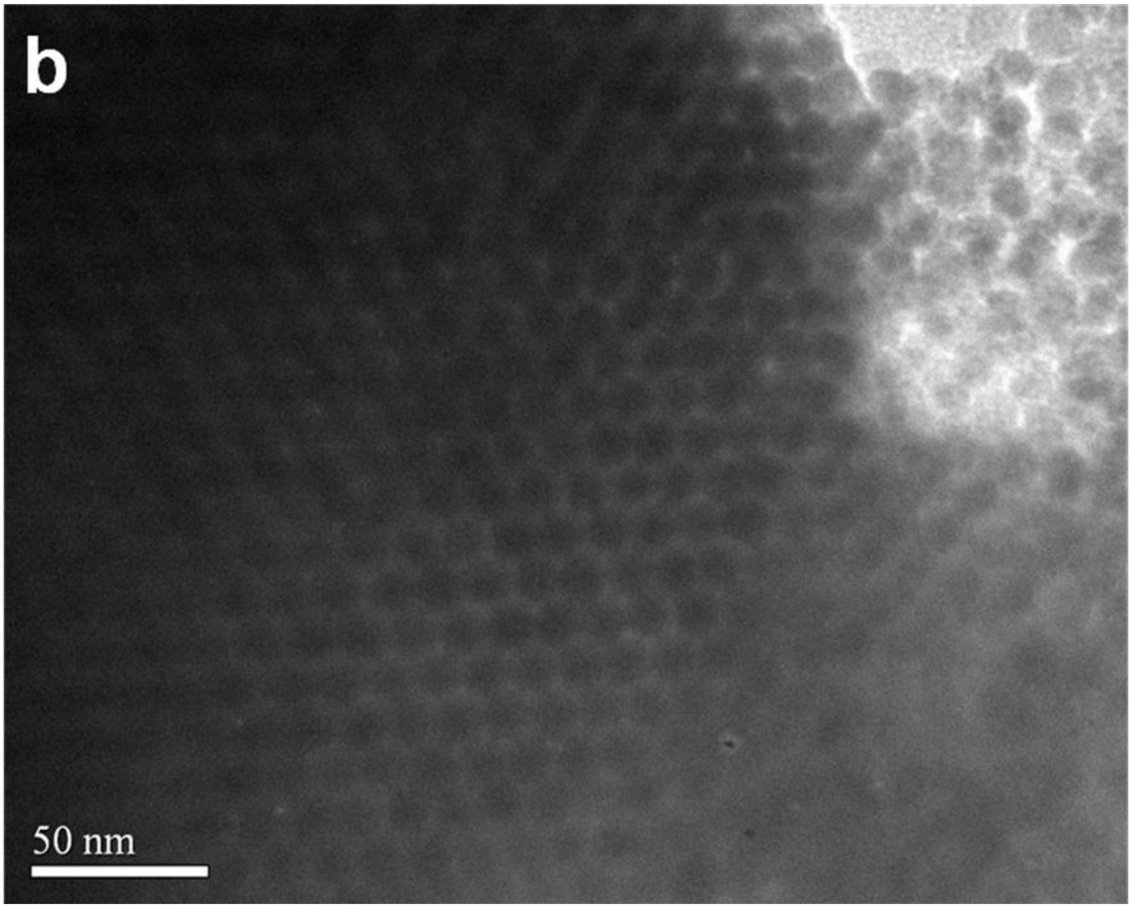




Notes: (a) Magnified TEM image (Figure 5f in the main text): Complex structures formed from Mn_3O_4 nanoplates, (b) schematic illustrations of zigzag structures assembled along both X and Y directions (upper drawing) and parallel arrangements assembled only along X direction (lower drawing), and (c) large SCs formed by the Mn_3O_4 nanoplates. The average thickness of nanoplates is ~4 nm. Therefore, the distance between two nanoplates is ~2 nm, which is close to the chain length of OLA.

Figure S6. Effects of solvent on self-assembly



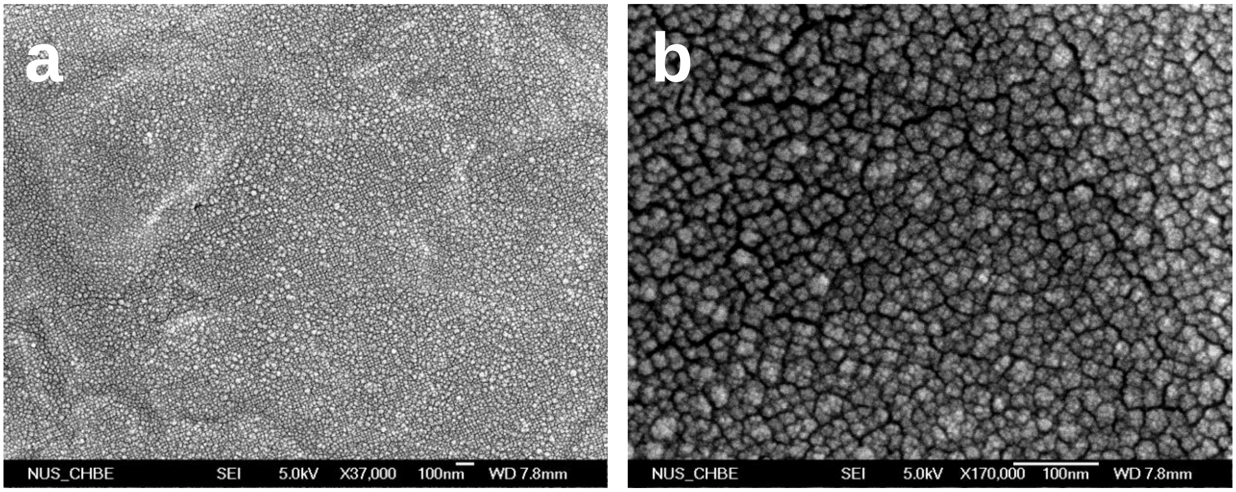


Notes: (a-b) TEM images of superlattices from two parallel experiments (washed with only ethanol). The concentration of MnAc in the synthesis of the sample in Figure 9c-d lies between Figure S6a and Figure S6b. Therefore, the sample of Figure 9c-d in the main text should also form SCs if no acetone involved in the washing process.

Experimental conditions:

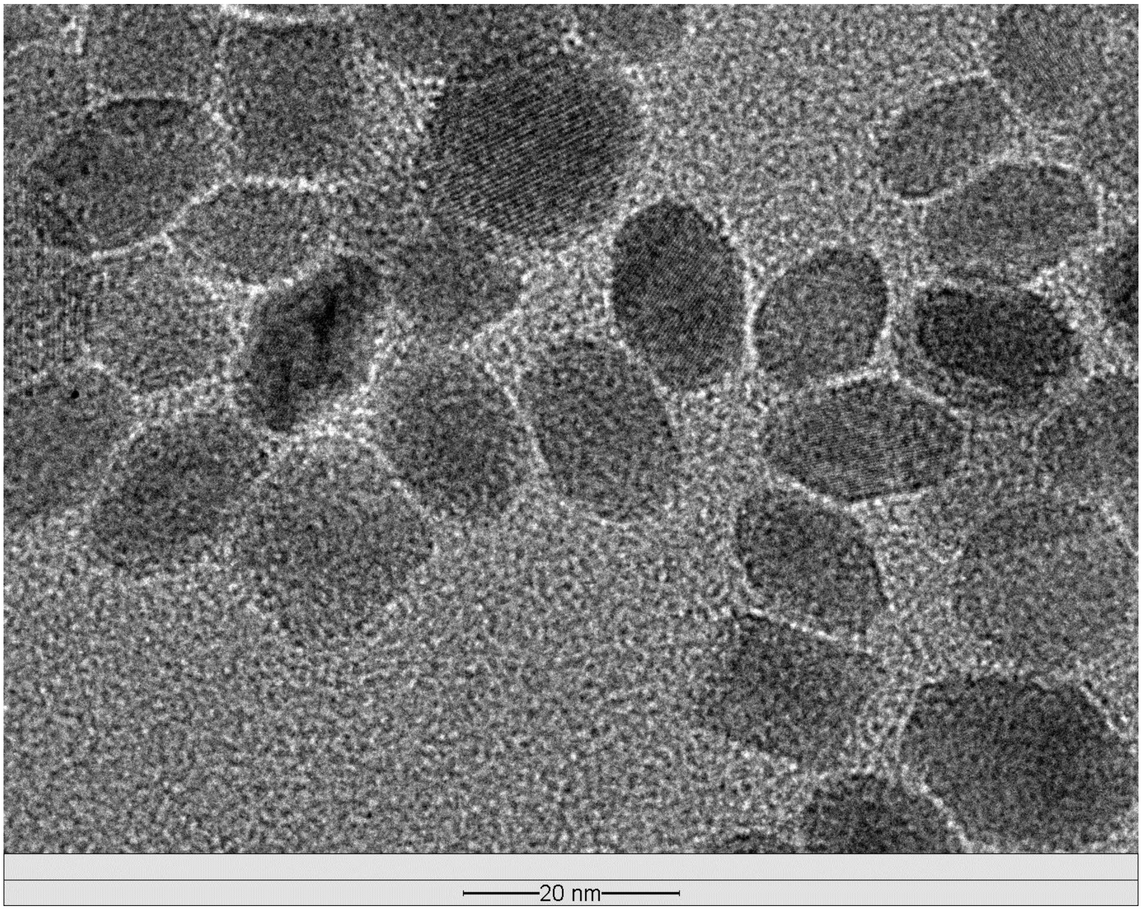
Figure S6a: 0.13 g of MnAc, 10 mL of 70% OLA; washed with ethanol.
Figure S6b: 0.42 g of MnAc, 10 mL of 80-90% OLA; washed with ethanol.
Figure 9c-d: 0.42 g of MnAc, 20 mL of 80-90% OLA; washed with acetone and ethanol.

Figure S7. FESEM images of Mn_3O_4 supracrystals



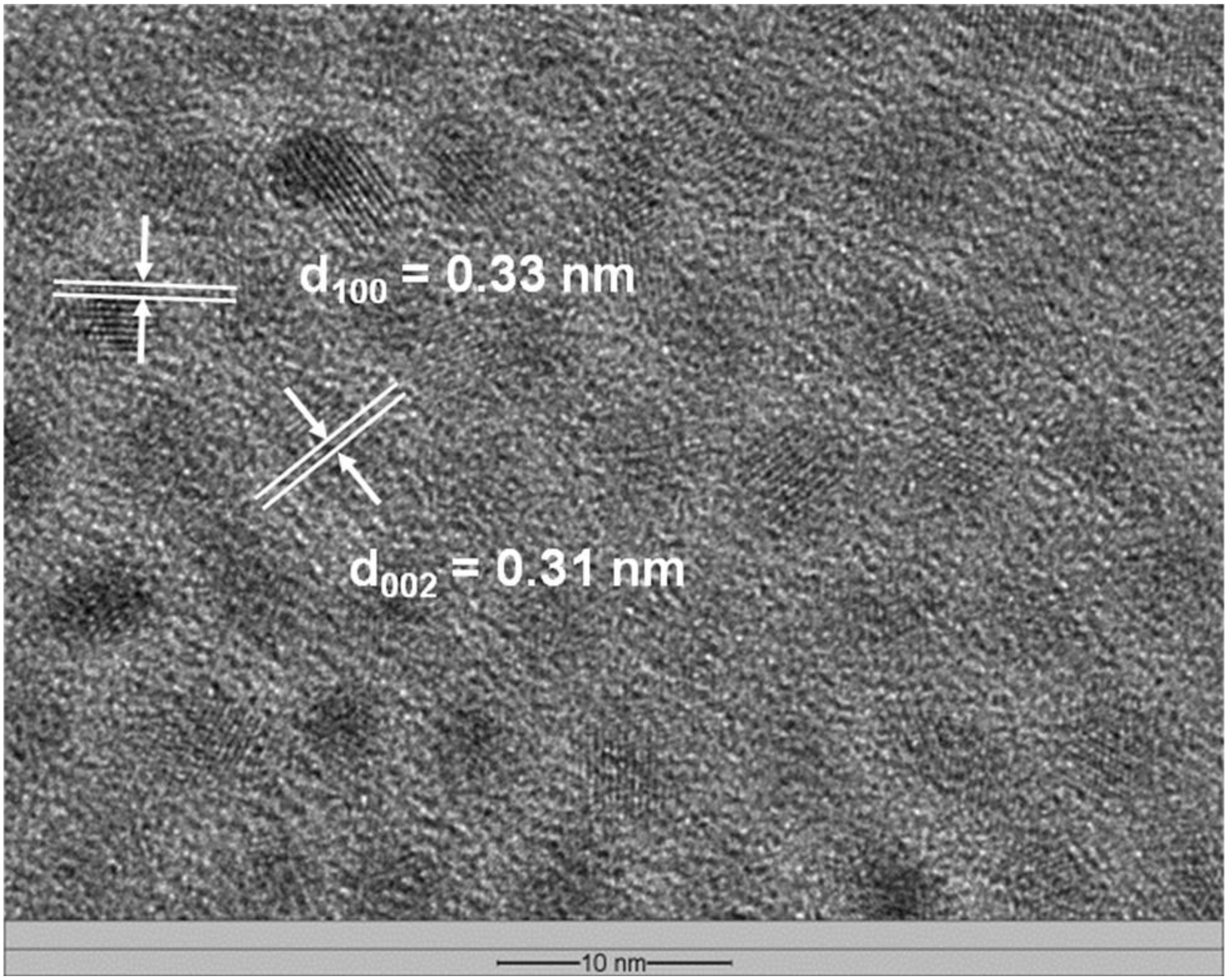
Notes: FESEM images of Figure 7a in the main text: (a) at lower magnification, and (b) at higher magnification. The large particles randomly scattered on top of two-dimensional SLs are Pt-coating employed in our FESEM measurement (to prevent charging effect at higher magnification).

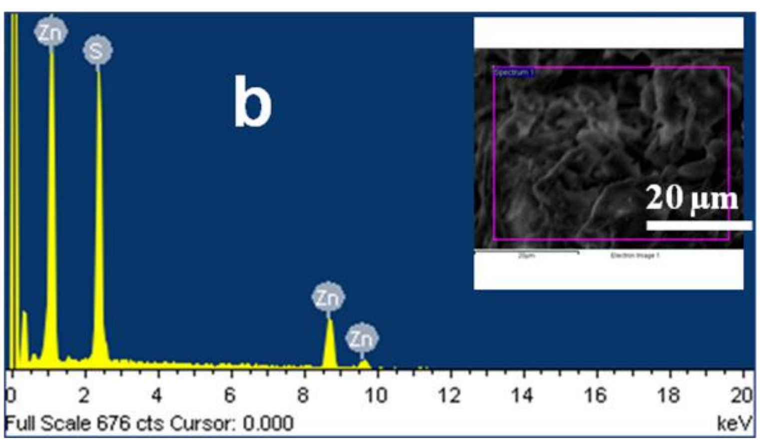
Figure S8. HRTEM image of less uniform Mn_3O_4 crystals



Note: There are several types of Mn_3O_4 nanocrystals in this sample.

Figure S9. Characterization of ZnS nanocrystals





Element	Weight%	Atomic%
S K	34.80	52.11
Zn L	65.20	47.89
Totals	100.00	

Notes: (a) HRTEM images show two lattice distances of 0.33 nm and 0.31 nm which correspond to the *d*-spacings of the (100) and (002) of ZnS respectively, and (b) EDX analysis shows that the ZnS nanocrystals indeed have a chemical composition of Zn:S = 1:1.