Supporting information

Scalable Assembly of Crystalline Binary Nanocrystal Superparticles and Their Enhanced Magnetic and Electrochemical Properties

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Table of Contents

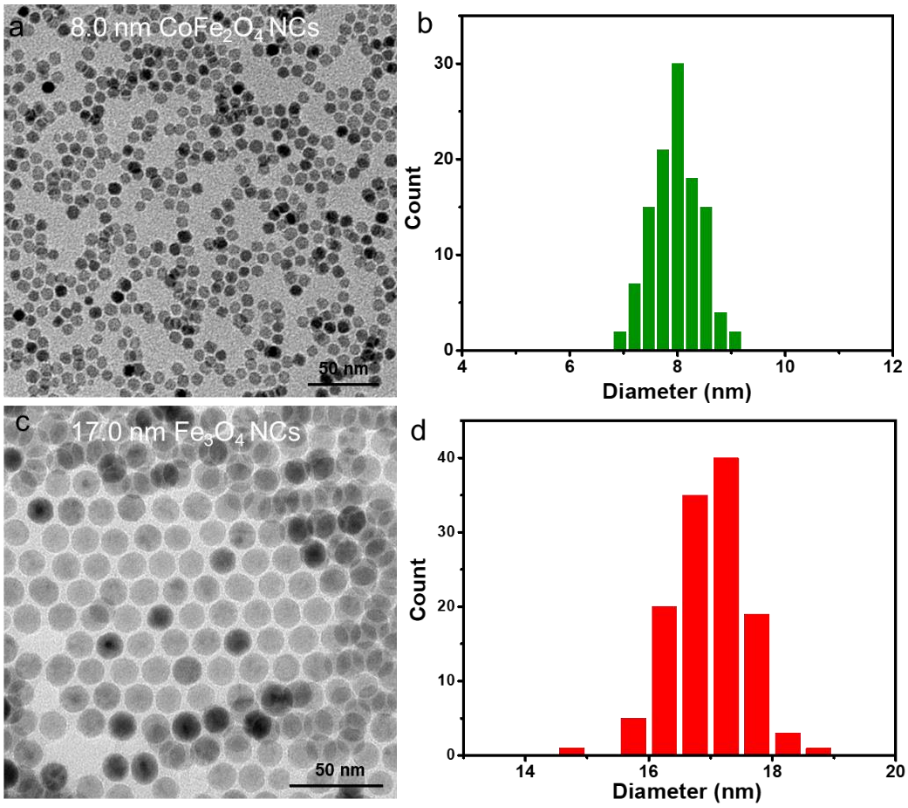

Figure S1. TEM images and the corresponding size distribution histograms of (a, b) 8.0 nm $CoFe_2O_4$ NCs and (c, d) 17.0 nm Fe_3O_4 NCs used for constructing AB_{13}-type binary superparticles.

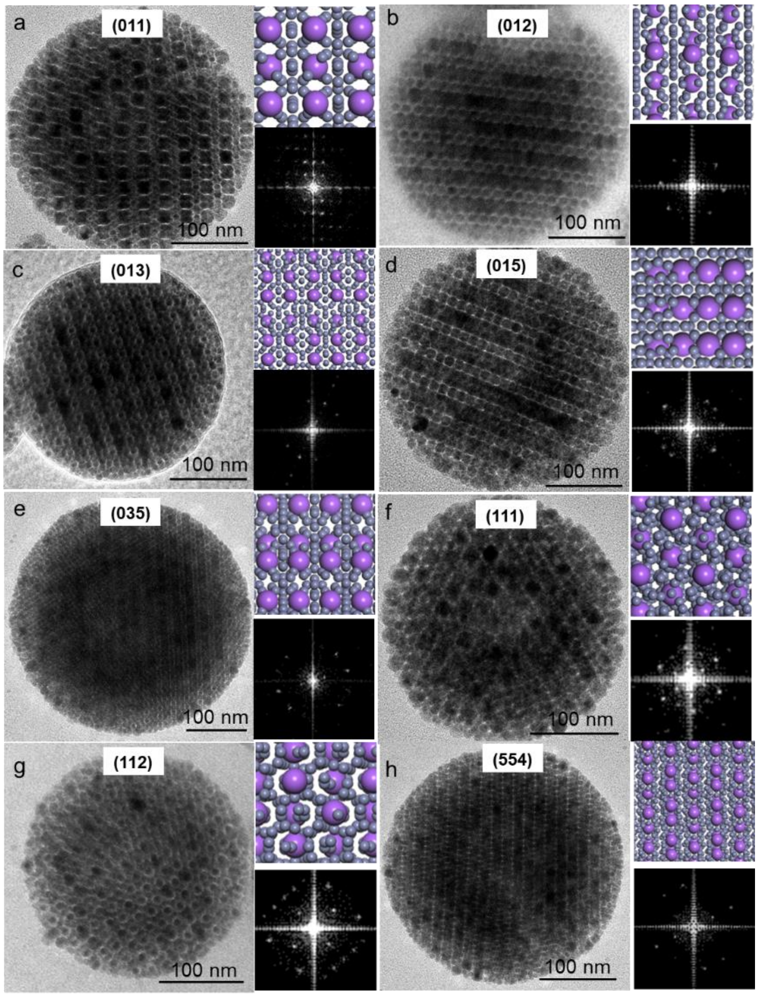

Figure S2. (a-h) TEM images and the corresponding crystallographic models and FFTs of AB_{13}-type $CoFe_2O_4$-Fe_3O_4 binary superparticles viewed from various lattice planes as indicated.

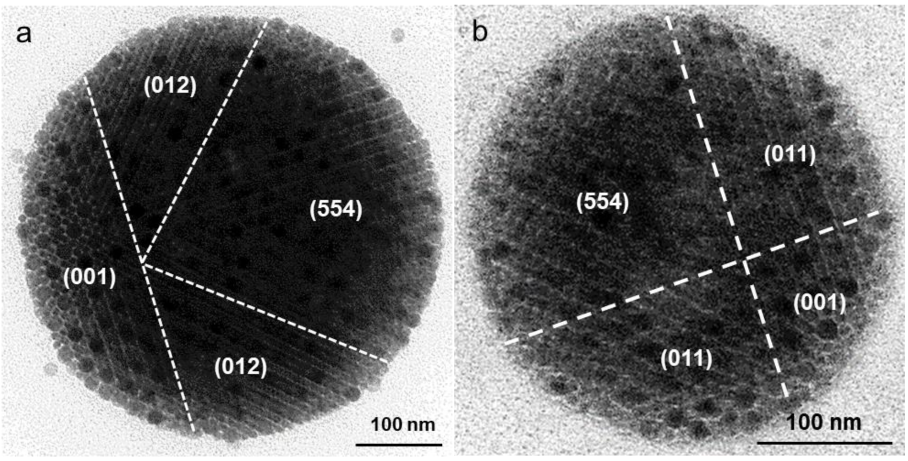

Figure S3. (a, b) TEM images of AB_{13}-type $CoFe_2O_4$-Fe_3O_4 binary superparticles with grain boundaries.

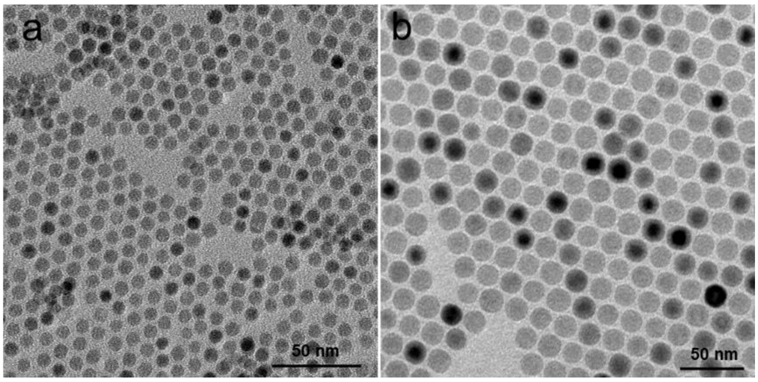

Figure S4. TEM images of (a) 8.5 nm and (b) 17.0 nm Fe_3O_4 NCs used for constructing AB_{13}-type Fe_3O_4-Fe_3O_4 binary superparticles.

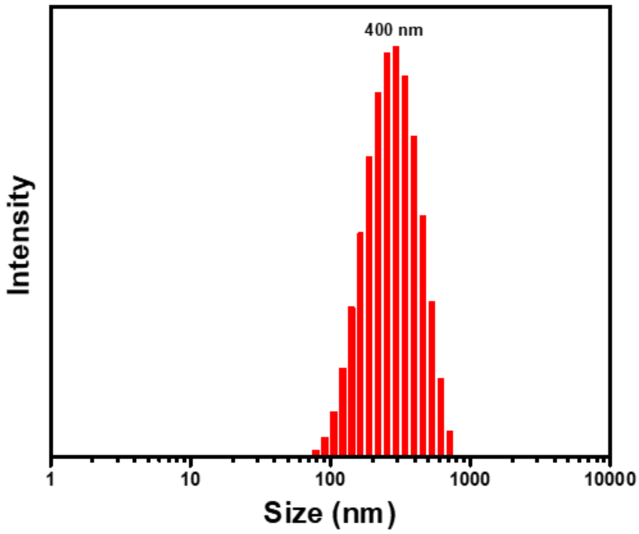

Figure S5. DLS measurements of AB_{13}-type Fe_3O_4-Fe_3O_4 BNSL colloids.

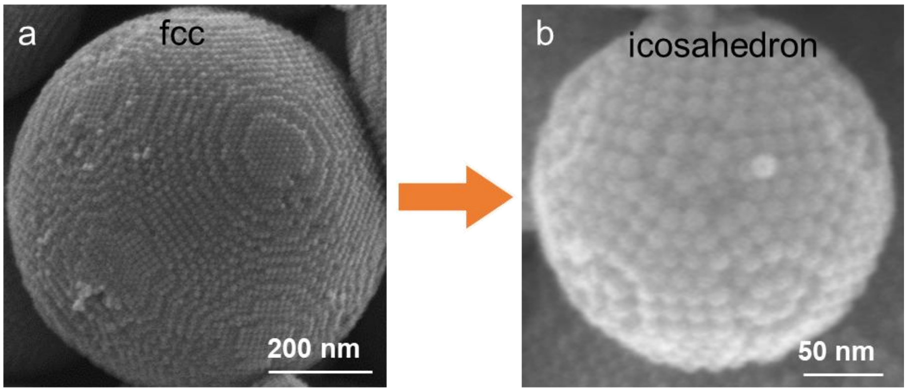

Figure S6. SEM images of single-component superparticles self-assembled from 17.0 nm Fe_3O_4 NCs, showing the transition from (a) *fcc* to (b) icosahedral symmetry as the superparticle size is reduced to ~200 nm.

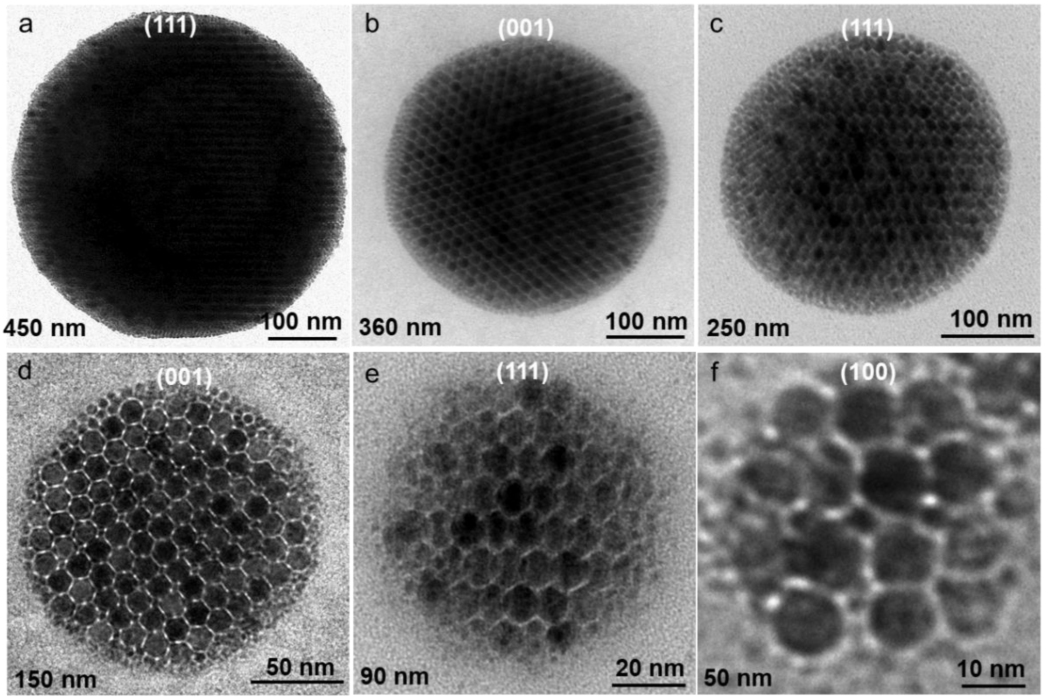

Figure S7. TEM images of a series of AlB_2-type binary superparticles with sizes gradually decreasing from 450 to 50 nm.

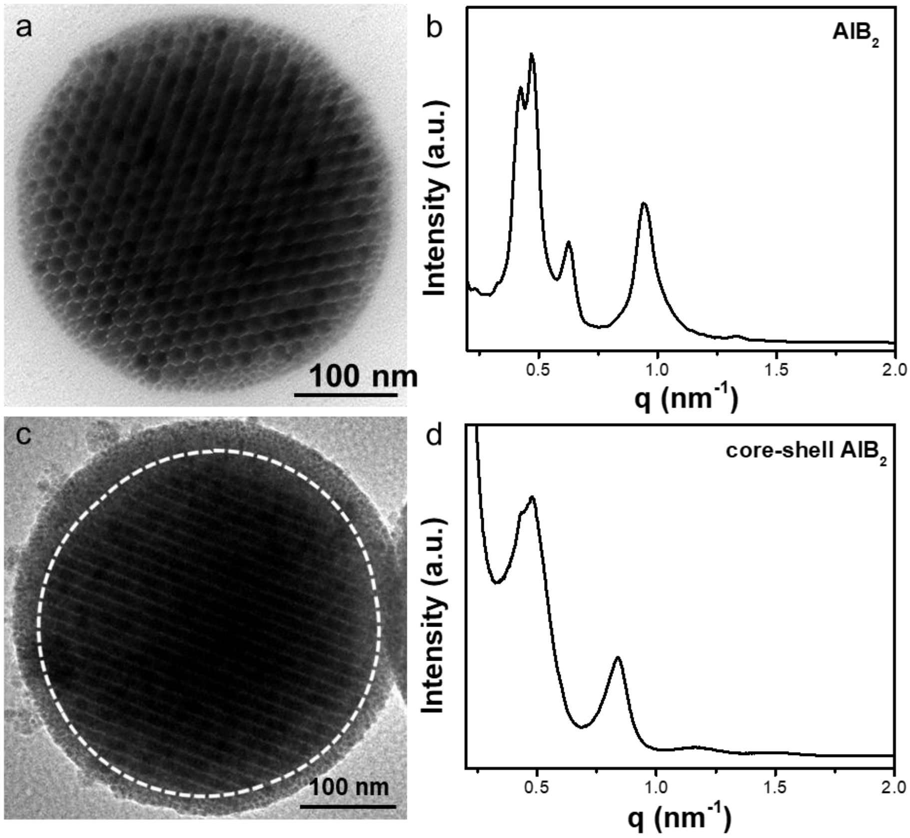

Figure S8. (a, b) TEM image and corresponding SAXS pattern of AlB_2-type binary superparticles self-assembled from 4.5 nm $CoFe_2O_4$ NCs and 11.0 nm Fe_3O_4 NCs with a number ratio of ~2:1. (c, d) TEM image and corresponding SAXS pattern of core-shell superparticles featuring AlB_2-type cores (as indicated by the dashed circle), which were self-assembled from 4.5 nm $CoFe_2O_4$ NCs and 11.0 nm Fe_3O_4 NCs with a number ratio of ~13:1.

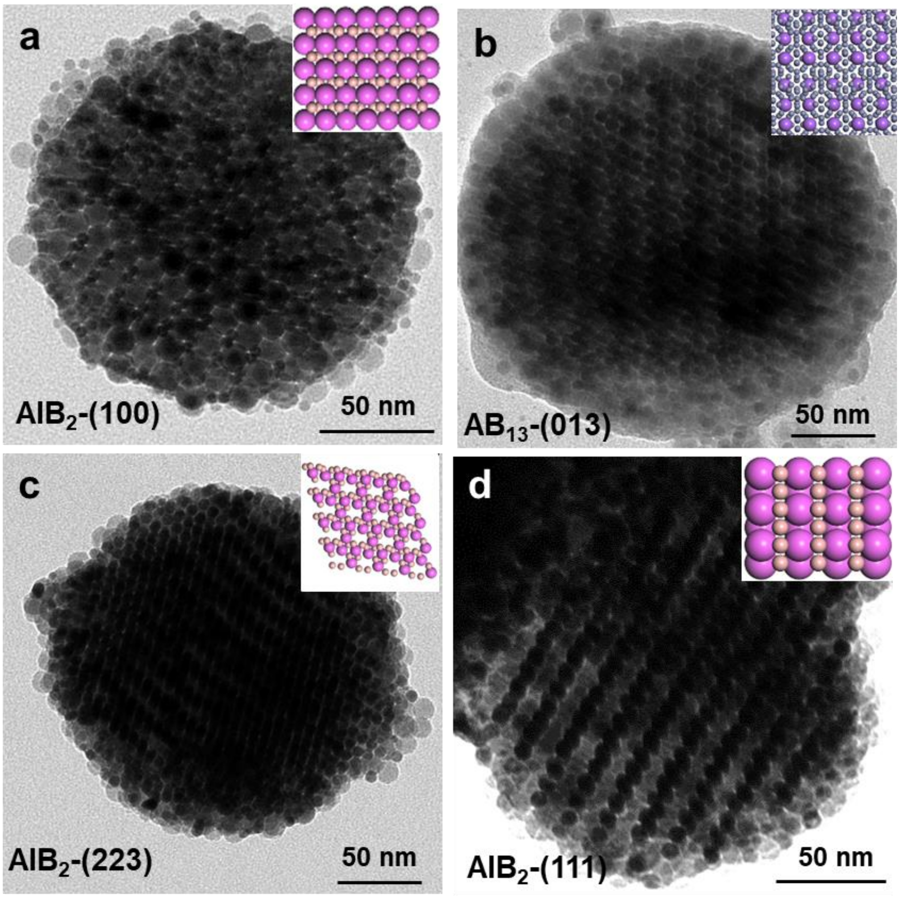

Figure S9. TEM images of binary superparticles with various structures and compositions: (a) AlB_2-type superparticles composed of 6.0 nm Pd NCs and 15.0 nm Fe_3O_4 NCs; (b) AB_{13}-type superparticles composed of 8.0 nm Pd NCs and 15.0 nm Fe_3O_4 NCs; (c) AlB_2-type superparticles composed of 7.0 nm Au NCs and 15.0 nm Fe_3O_4 NCs onto the (223) lattice plane; (d) AlB_2-type superparticles composed of 7.0 nm Au NCs and 15.0 nm Fe_3O_4 NCs onto the (111) lattice plane. Insets show the corresponding crystallographic models.

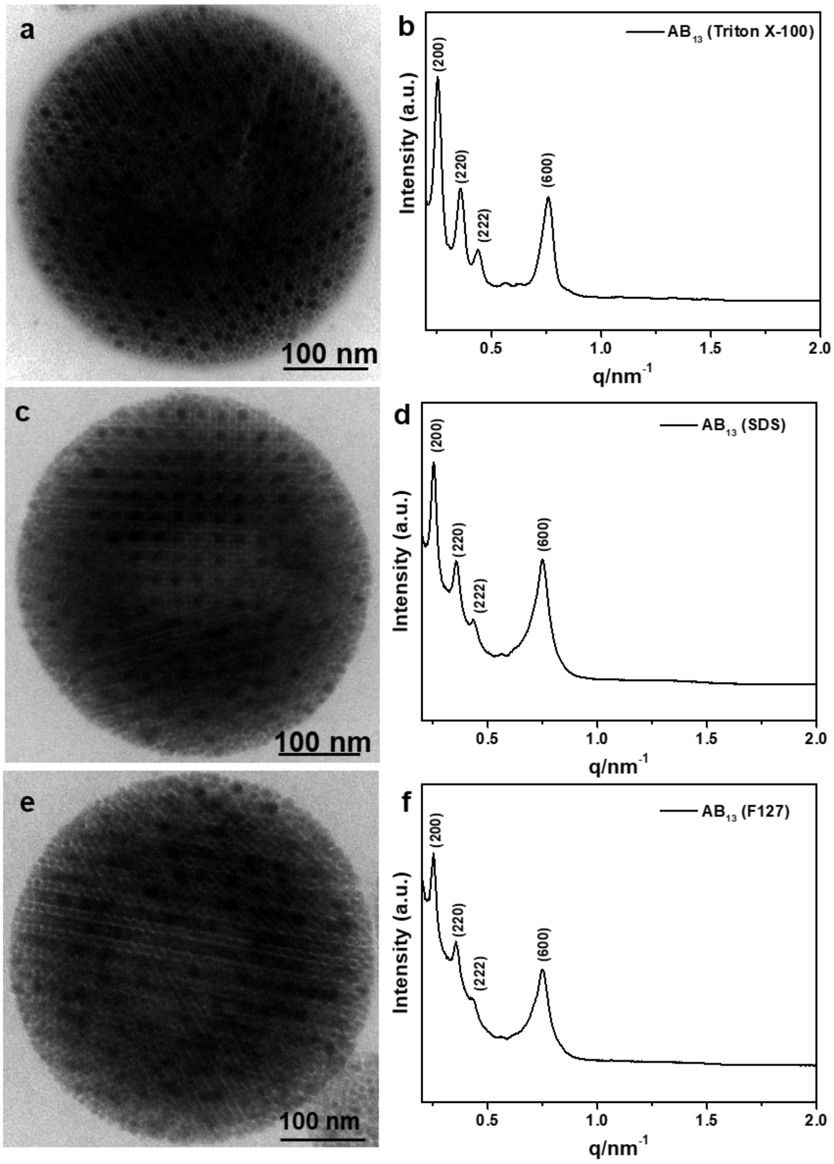

Figure S10. TEM image and the corresponding SAXS patterns of AB_{13}-type $CoFe_2O_4$-Fe_3O_4 binary superparticles self-assembled with the assistance of different surfactants: (a, b) Triton X-100, (c, d) SDS, and (e, f) F127.

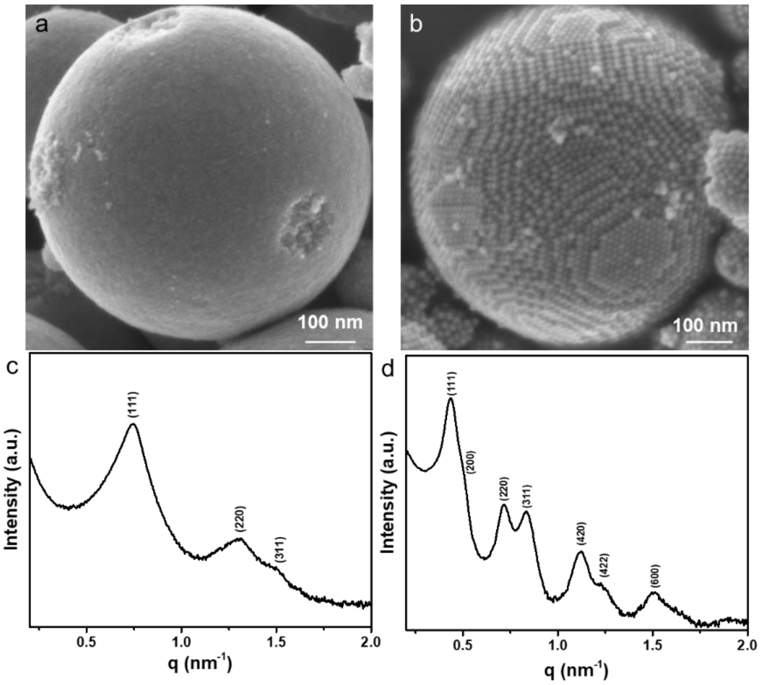

Figure S11. SEM images and the corresponding SAXS patterns of *fcc* superparticles composed of (a, c) 8.0 nm $CoFe_2O_4$ NCs and (b, d) 17.0 nm Fe_3O_4 NCs.

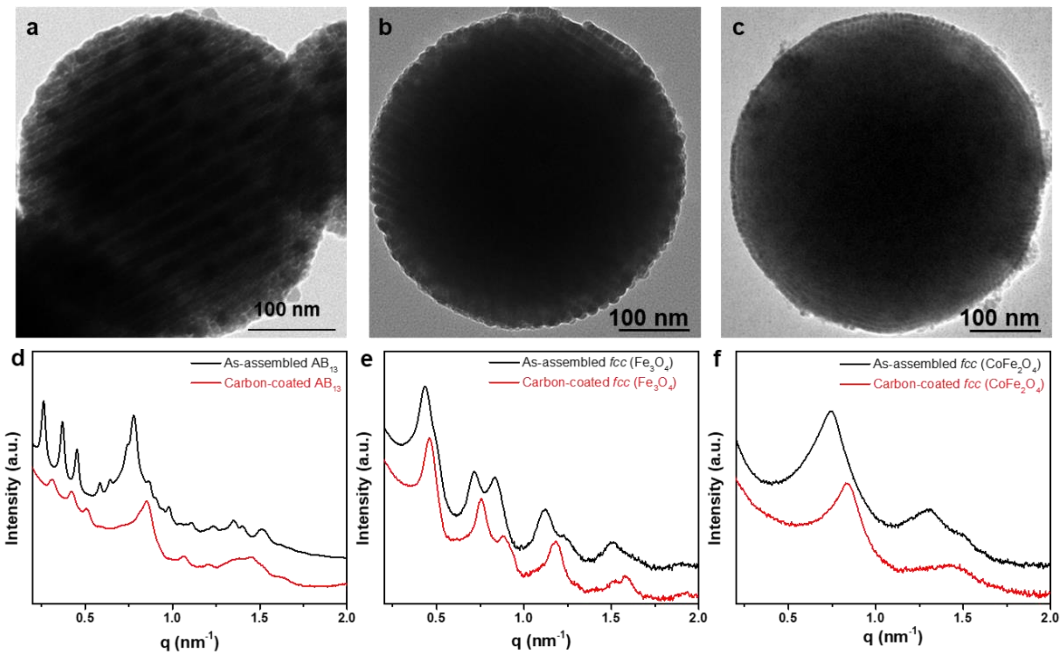

Figure S12. TEM images and the corresponding SAXS patterns of various superparticles after ligand carbonization: (a, d) carbon-coated AB_{13}-type binary superparticles composed of 8.0 nm $CoFe_2O_4$ and 17.0 nm Fe_3O_4 NCs; (b, e) carbon-coated *fcc* superparticles of 17.0 nm Fe_3O_4 NCs; (c, f) carbon-coated *fcc* superparticles of 8.0 nm $CoFe_2O_4$ NCs. For each type of superparticles, the SAXS patterns before ligand carbonization were also provided in (d-f) for comparison. For all sample, the peaks were systematically shifted toward high angles after ligand carbonization, suggesting the occurrence of lattice contract.

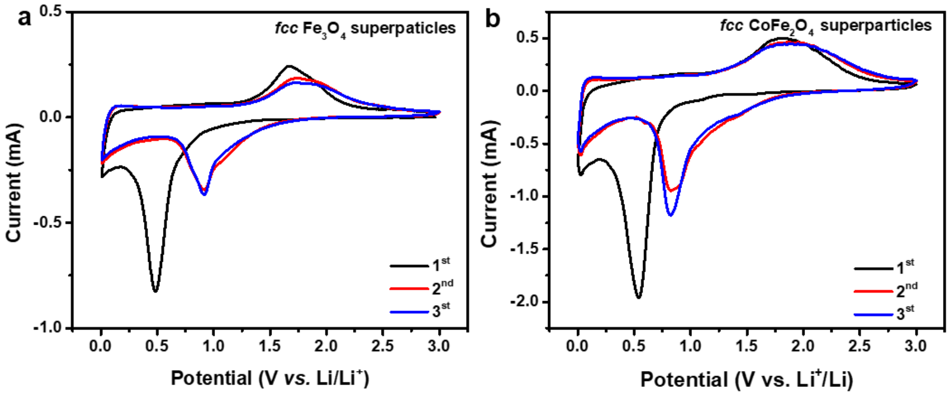

Figure S13. Representative CV curves of *fcc* superparticles composed of (a) 17.0 nm Fe_3O_4 NCs and (b) 8.0 nm $CoFe_2O_4$ NCs, respectively.

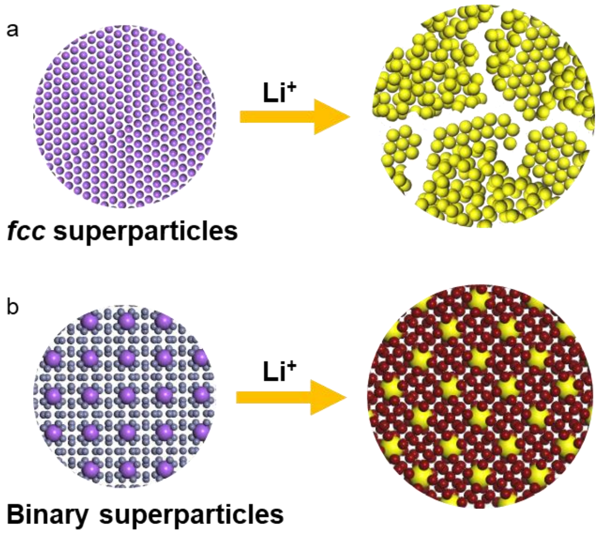

Figure S14. Cross-sectional illustration depicting the structural evolution of (a) *fcc* superparticles and (b) binary superparticles during electrochemical lithiation.

Table S1. Reaction conditions for growing monodisperse Fe_3O_4 NCs with different sizes.

NC size	Solvent	$Fe(OA)_3$	OA	Temperature (ºC)
20.0 nm	50 g ODE	9.0 g	2.0 g	325
17.0 nm	50 g ODE	9.0 g	2.0 g	320
15.0 nm	50 g ODE	9.0 g	2.0 g	318
11.0 nm	10 g TDE/40 g ODE	9.0 g	2.0 g	300
9.0 nm	17.5 g TDE/32.5 g ODE	9.0 g	1.5 g	290
8.5 nm	50 g HDE	9.0 g	2.0 g	290
7.0 nm	50 g HDE	9.0 g	2.0 g	288
6.5 nm	10 g TDE/40 g HDE	9.0 g	2.0 g	280

Table S2. NC formulation for the growth of various BNSL colloids (The concentration of all NCs is 75 mg mL^{-1} unless noted).

Lattice structure	Volume of large NCs	Volume of small NCs
AB_{13}	8.0 mL 17.0 nm Fe_3O_4	12.0 mL 8.0 nm $CoFe_2O_4$
AB_{13}	8.0 mL 17.0 nm Fe_3O_4	12.0 mL 8.5 nm Fe_3O_4
AB_{13}	8.0 mL 20.0 nm Fe_3O_4	12.0 mL 9.0 nm $CoFe_2O_4$
AlB_2	15.0 mL 11.0 nm Fe_3O_4	5.0 mL 4.5 nm $CoFe_2O_4$
AlB_2	15.0 mL 15.0 nm Fe_3O_4	5.0 mL 7.0 nm Fe_3O_4
$MgZn_2$	12.0 mL 6.5 nm Fe_3O_4	8.0 mL 4.5 nm $CoFe_2O_4$
$MgZn_2$	12.0 mL 9.0 nm Fe_3O_4	8.0 mL 6.5 nm Fe_3O_4
NaCl	19.0 mL 15.0 nm Fe_3O_4	1.0 mL 4.5 nm $CoFe_2O_4$
$CaCu_5$	9.0 mL 7.0 nm Fe_3O_4	11.0 mL 4.5 nm $CoFe_2O_4$
AB_{13}	0.2 mL 15.0 nm Fe_3O_4	0.8 mL 8.0 nm Pd (20 mg mL^{-1})
AlB_2	0.45 mL 15.0 nm Fe_3O_4	0.55 mL 6.0 nm Pd (20 mg mL^{-1})
AlB_2	0.25 mL 15.0 nm Fe_3O_4	0.75 mL 7.0 nm Au (20 mg mL^{-1})

Table S3. The leached Fe and Co contents in the electrolyte after cycling.

Anodes	Fe (ppm)	Fe mass loss percentage (%)	Co (ppm)	Co mass loss percentage (%)
AB_{13} binary superparticles	70	1.7	4	0.3
fcc $CoFe_2O_4$ superparticles	172	4.8	28	1.5
fcc Fe_3O_4 superparticles	442	8.3	None	None

Calculation of the packing fraction of carbon-coated AB_{13}-type $CoFe_2O_4$-Fe_3O_4 binary superparticles

1. Determination of the carbon shell thickness in fcc superparticles of 17.0 nm Fe_3O_4 NCs:

According to SAXS, the lattice constant (a) of *fcc* superparticles of 17.0 nm Fe_3O_4 NCs is calculated to be $a = \frac{2\pi\sqrt{h^2+k^2+l^2}}{q}$ = 24.6 nm, were h, k, and l are Miller's indices and q is the scattering vector.

The volume of a unit cell, $Volume_{\text{(unit cell)}}$, is calculated as below:

$Volume_{\text{(unit cell)}} = a^3 = (24.6\ \text{nm})^3 = 14887\ \text{nm}^3$.

Since the theoretical packing fraction of *fcc* superparticles is 74%, the carbon shell thickness ($L1$) surrounding individual Fe_3O_4 NCs is calculated to be 0.2 nm by the equation $\frac{Volume\ \text{(NC + carbon shell)}}{Volume\ \text{(unit cell)}} = \frac{4\pi}{3} \times \frac{4(8.5+L1)^3}{14887} = 74\%$.

2. Determination of the carbon shell thickness in fcc superparticles of 8.0 nm $CoFe_2O_4$ NCs:

According to SAXS, the lattice constant (a) of *fcc* superparticles of 8.0 nm $CoFe_2O_4$ NCs is calculated to be $a = \frac{2\pi\sqrt{h^2+k^2+l^2}}{q}$ = 11.9 nm.

The volume of a unit cell, $Volume_{\text{(unit cell)}}$, is calculated as below:

$Volume_{\text{(unit cell)}} = a^3 = (11.9\ \text{nm})^3 = 1685\ \text{nm}^3$.

Similar to *fcc* Fe_3O_4 superparticles, the carbon shell thickness $L2$ is calculated to be 0.2 nm by the equation $\frac{Volume\ \text{(NCs + carbon shell)}}{Volume\ \text{(unit cell)}} = \frac{4\pi}{3} \times \frac{4(4.0+L2)^3}{1685} = 74\%$

3. Calculation of the packing fraction of carbon-coated AB_{13} superparticles:

According to SAXS, the lattice constant (a) of AB_{13}-type $CoFe_2O_4$-Fe_3O_4 binary superparticles is calculated to be $a = \frac{2\pi\sqrt{h^2+k^2+l^2}}{q}$ = 42.9 nm.

The volume of a unit cell, $Volume_{\text{(unit cell)}}$, is calculated as below:

$Volume_{\text{(unit cell)}} = a^3 = (42.9\ \text{nm})^3 = 78954\ \text{nm}^3$.

Assuming that the carbon shells surrounding 17.0 nm Fe_3O_4 NCs and 8.0 nm $CoFe_2O_4$ NCs in binary superparticles are the same as *L1* and *L2* in thickness, the packing fraction of carbon-coated AB_{13} superparticles can be calculated as below:

$$packing\ fraction = \frac{Volume\ \text{(NCs + carbon shell)}}{Volume\ \text{(unit cell)}} = \frac{4\pi}{3} \times \frac{8(8.5+L1)^3+104(4.0+L2)^3}{78954} = 69\%.$$