Controlled synthesis of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ concave nanocubes and highly branched cubic mesocrystals

Zhenhu Li, Yurong Ma* and Limin Qi*

Supporting Information

Fig. S1. TEM images of one of the Mn$_{0.15}$Fe$_{0.85}$O concave nanocubes (Fig. 1) recorded after tilting the sample holder to different angles.

Fig. S2. Characterizations on the Mn$_x$Fe$_{3-x}$O$_4$ concave nanocubes obtained while the Mn$_{0.13}$Fe$_{0.87}$O concave nanocubes were exposed to air for 2 hours at 200 °C. (a) TEM image and corresponding SAED pattern, (b) XRD pattern, and (c) Magnetic hysteresis loops.
Fig. S3 TEM images of Mn$_{0.15}$Fe$_{0.85}$O NPs obtained with different volume ratios of OA to OAm (ROA/OAm) while remaining the total volume of OA and OAm as 10 mL. The insets show the corresponding SAED patterns. The R$_{OA/OAm}$ values are as follows: (a) 1.25, (b) 0.9, (c) 0.8, (d) 0.67.

Fig. S4 Characterizations in details on Mn$_{0.15}$Fe$_{0.85}$O concave nanocubes obtained with the concentration sum of metal precursors 0.18 mol/L and heating rate of 5 °C/min (Fig. 3c), (a) TEM, (b, c) high resolution TEM images, (Inset: FFTs of the marked areas corresponding to the red and white boxes, respectively) (d) a HAADF-STEM image, and (e, f) Mn and Fe mappings of a Mn$_{0.15}$Fe$_{0.85}$O concave nanocubes.
Fig. S5 TEM images of one of the Mn$_{0.15}$Fe$_{0.85}$O concave nanocubes obtained with the concentration sum of metal precursors 0.18 mol/L and heating rate of 5 °C/min (Fig. 3c) recorded after tilting the sample holder in-situ to different angles.

Fig. S6 The relation of the Mn contents (x) and the saturation magnetization (Ms) and coercive field values (Hc) of the obtained Mn$_x$Fe$_{1-x}$O nanoparticles characterized at 2 T and 5 K.
Fig. S7 TEM images of Mn$_{0.15}$Fe$_{0.85}$O nanoparticles obtained when the heating time for the first step heating process at 200°C was varied from 0 to 60 min while keeping the second step heating time at 300 °C to be 60 min. The insets show the corresponding SAED patterns. (a) 0, (b) 10 min, (c) 30 min, (d) 40 min.

Scheme S1. Schematic illustration of the formation mechanism for the Mn$_x$Fe$_{1-x}$O concave nanocubes.
Fig. S8. TEM images of one of the highly branched cubic Mn$_{0.15}$Fe$_{0.85}$O mesocrystals (Fig. 7) recorded after tilting the sample holder to different angles. The SAED pattern related to the image obtained at -40° shows crystal facets indexes in white and red corresponding to Mn$_x$Fe$_{1-x}$O rock salt phase and Mn$_x$Fe$_{3-x}$O$_4$ spinel phases, respectively).

Fig. S9. TEM images of one of the highly branched cubic Mn$_{0.15}$Fe$_{0.85}$O mesocrystals after aging at 300 °C for 30 min (Fig. 8c) recorded after tilting the sample holder to different angles. The inset in (a) shows the SAED pattern.
corresponding to planes of Mn\textsubscript{x}Fe\textsubscript{1-x}O rock salt phase.

Fig. S10 TEM images of the highly branched cubic Mn\textsubscript{0.15}Fe\textsubscript{0.85}O mesocrystals after aging at 300 °C for 120 min. (b-d) TEM of one Mn\textsubscript{0.15}Fe\textsubscript{0.85}O mesocrystal recorded after tilting the sample holder to different angles. The inset in (b) shows the SAED pattern with crystal facets indexes in white and red corresponding to Mn\textsubscript{x}Fe\textsubscript{1-x}O rock salt phase and Mn\textsubscript{x}Fe\textsubscript{3-x}O\textsubscript{4} spinel phases, respectively.

Fig. S11 TEM images of the highly branched cubic Mn\textsubscript{0.15}Fe\textsubscript{0.85}O mesocrystals obtained in the presence of different amounts of 1-octadecene, (a-c) 2.5 ml, (d-f) 7.5 ml. The insets in (b) and (e) show the relative SAED patterns with crystal facets indexes in white and red corresponding to Mn\textsubscript{x}Fe\textsubscript{1-x}O rock salt phase and Mn\textsubscript{x}Fe\textsubscript{3-x}O\textsubscript{4}.
spinel phases, respectively. The images in (c) and (f) were obtained after tilting the mesocrystals in (b) and (e) to different angles, respectively.