Electronic Supplementary Information

Revisiting the Coordination Chemistry for Preparing Manganese Oxide Nanocrystals in the Presence of Oleylamine and Oleic Acid

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To identify the crystalline structure of the tiny spherical particles shown in Figure 1b, SAED and HRTEM measurements were carried out. The results shown in **Figure S1** suggest the tiny spherical particles are tetragonal Mn_3O_4.

The four-arm branched particles shown in Figure 1e also appeared as six-arm stars and even formed self-organized superstructures as shown in **Figure S2**.

The nanoparticles obtained after incubating the reaction mixture of $Mn(Ac)_2$ and oleylamine at a molar ratio of 1:10 at 100 °C under N_2 atmosphere for 9 h and the corresponding electron diffraction results are shown in **Figure S3**.

By quickly heating a stock solution containing $Mn(Ac)_2$, oleylamine, oleic acid, and ODE up to 250 °C within 17 min, particles with an average size of 4.2 nm were obtained at 250 °C at a reaction time of 20 min. The TEM results are provided in **Figure S4**.

The temporal evolution of size and size distribution of Mn_3O_4 and MnO nanocrystals formed in the system yielding branched MnO nanocrystals (Figure 1e) upon prolonged reaction are shown in **Figure S5**.

The temporal evolutions of size and size distribution of Mn_3O_4 and MnO nanocrystals obtained upon a post-treatment of the branched MnO nanocrystals in oleylamine are shown in **Figure S6.**

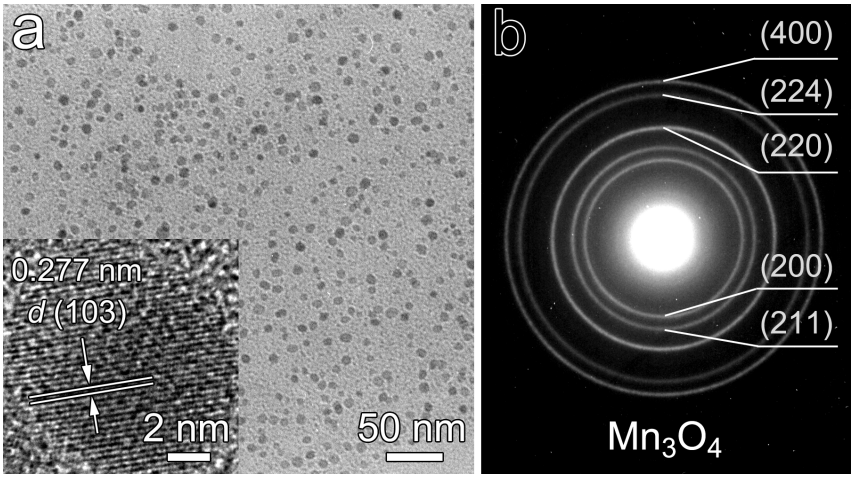

Figure S1. TEM image (a) of the tiny particles shown in Figure 1b together with the corresponding electron diffraction patterns (b). Inset: HRTEM image of an individual particle overlaid with crystal plane identifications according to JCPDS card (24-0734) for tetragonal Mn_3O_4. The diffraction rings are labeled with Miller indices according to standard data for tetragonal Mn_3O_4.

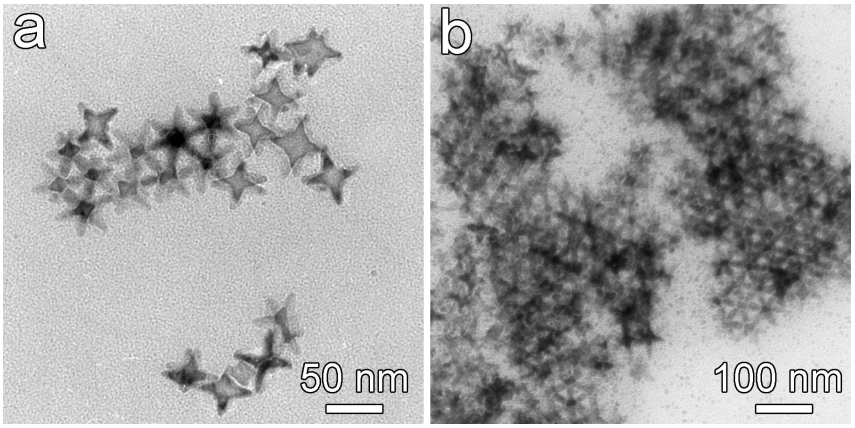

Figure S2. TEM images of branched particles showing self-organized superstructures in some locations on the TEM grid.

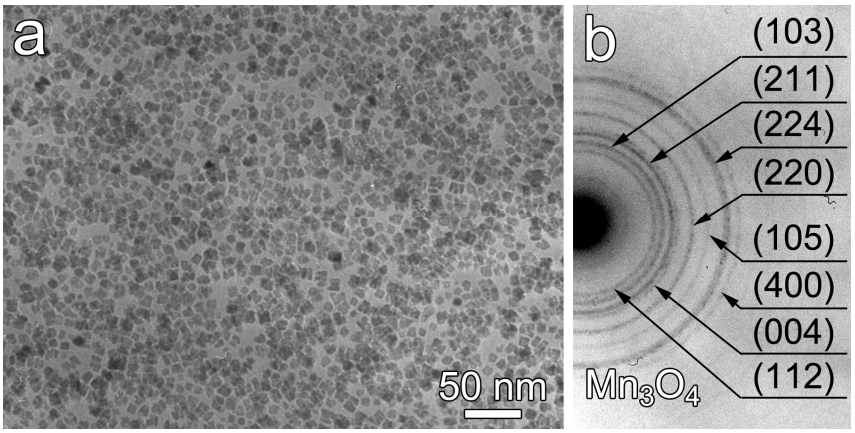

Figure S3. TEM image (a) of the particles obtained by pyrolysis of $Mn(Ac)_2$ in oleylamine at 100 °C for 9 h together with the corresponding electron diffraction pattern (b). The diffraction rings are labeled with Miller indices according to tetragonal Mn_3O_4 (JCPDS 24-0734).

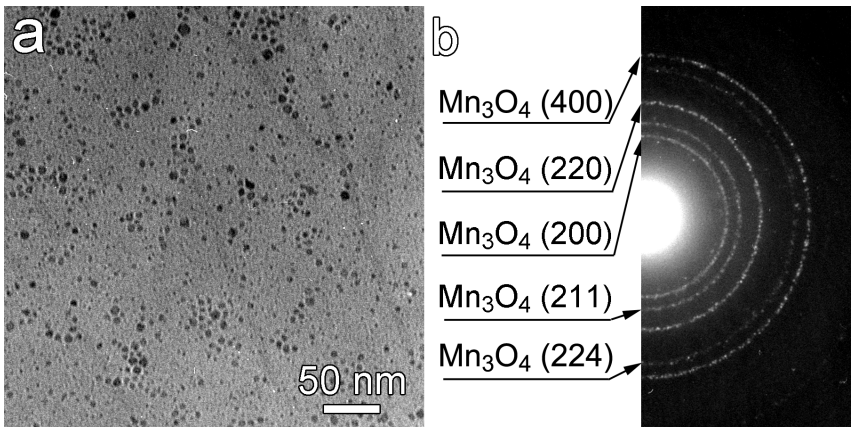

Figure S4. TEM image (a) and the corresponding electron diffraction pattern (b) of the particles obtained by pyrolysis of $Mn(Ac)_2$ in ODE containing oleylamine and oleic acid at 250 °C for 20 min upon directly heating the reaction mixture up to 250 °C within 17 min. The diffraction rings are labeled with Miller indices according to tetragonal Mn_3O_4 (JCPDS 24-0734).

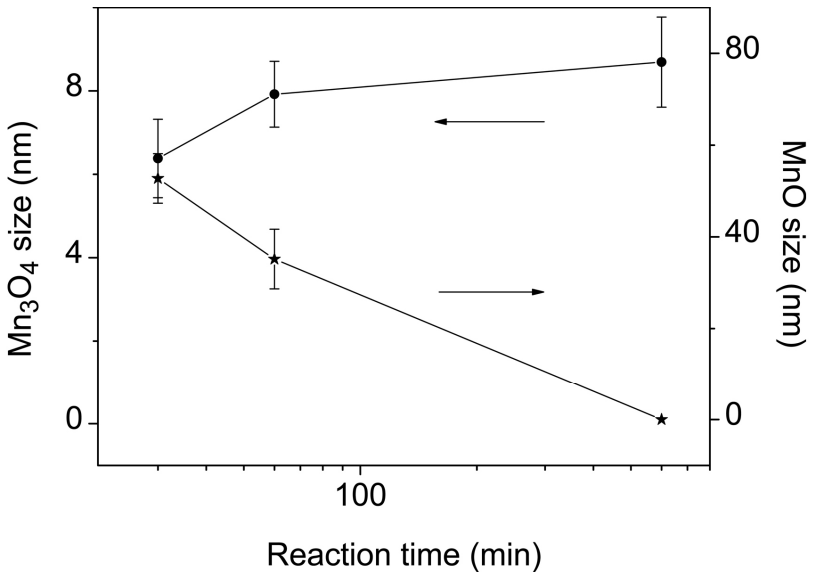

Figure S5. Temporal evolution of size and size distribution of Mn_3O_4 and MnO nanocrystals formed in the system yielding branched MnO nanocrystals (Figure 1e) upon prolonged reaction.

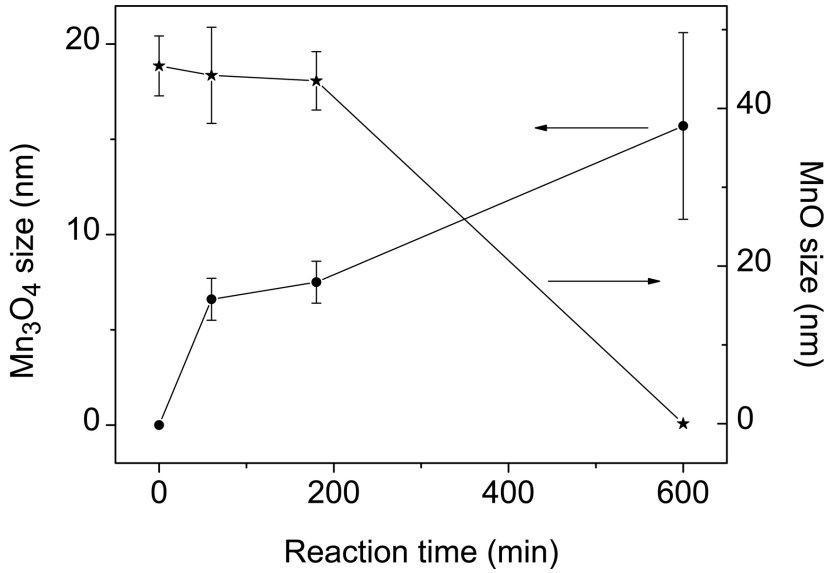

Figure S6. Temporal evolutions of size and size distribution of Mn_3O_4 and MnO nanocrystals obtained upon a post-treatment of the branched MnO nanocrystals in oleylamine.