Electronic Supplementary Information

Large-scale one pot synthesis of metal oxide nanoparticles by decomposition of metal carbonates or nitrates

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Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200 kV and TECNAI G2 F30 operated at 300 kV. X-ray diffraction (XRD) patterns were collected with a Rigaku Ultima III diffractometer system using a graphite-monochromatized Cu-K α radiation at 40 kV and 40 mA.CO_2 release was measured by using an infrared CO_2 sensor (Wohler KM410). Fast atom bombardment (FAB) ionization and double-focusing high-resolution magnetic sector mass analysis was performed by a DFS (Thermo Scientific, Germany) operated at acceleration voltage 5 kV, emission current 0.01 mA and electron energy -20 eV. 3-nitrobenzyl alcohol was used as a liquid matrix for fast atom bombardment ionization.

Experimental Section

Preparation of octahedral MnO nanoparticles

A mixture of bulk Mn precursor ($MnCO_3$ or $Mn(NO_3)_2$, 87 mmol) and oleic acid (90%, Sigma-Aldrich, 150 mL, 0.48 mol) was prepared in 1L 2-necked round-bottom flask equipped with a reflux condenser. The reaction mixture was heated to 330 ^oC (~15 ^oC min^{-1}) in a heating mantle with magnetic stirring under N_2 blanket (N_2 was blown at the flow rate of 100 mL min^{-1}). The solution gradually became transparent due to the decomposition of $MnCO_3$ over the reaction period of 30 min. A mixture of trioctylamine and oleylamine (the amounts are listed in Table S1) was subsequently added into the solution, and the solution colour became green due to the formation of MnO nanoparticles. After 1 h of heating at 330 ^oC, brown precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added excess ethanol.

run	oleic acid (mol)	TOA (mol)	oleylamine (mol)	diameter (nm)
1	0.48	0.48	0	20±2.5
2		0.53	0	25±2.0
3		0.58	0	29±1.8
4		0.43	0.05	38±2.1
5		0.34	0.14	80±20
6		0.24	0.24	200±32

Table S1. Reaction parameters used in the synthesis of size controlled octahedral MnO nanoparticles.

Preparation of multipod MnO nanoparticles

A mixture of bulk $MnCO_3$ powder (10 g, 87 mmol) and oleic acid (90%, Sigma-Aldrich, 150 mL, 0.48 mol) was prepared in 1L 2-necked round-bottom flask equipped with a reflux condenser. The reaction mixture was heated to 330 ^oC (~15 ^oC min^{-1}) in a heating mantle with magnetic stirring under N_2 blanket (N_2 was blown at the flow rate of 100 mL min^{-1}). After the solution became transparent, a mixture of trioctylamine (0.24 mol) and oleylamine (0.24 mol) was subsequently added into the solution. After 20 min from green coloured MnO formation, oleic acid (87 mmol) was added into the solution and kept for 30 min. Finally, brown precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added excess ethanol.

Preparation of Fe_3O_4 and CoO nanoparticles

Bulk metal precursor powder ($FeCO_3$, $CoCO_3$, $Fe(NO_3)_2$ or $Co(NO_3)_2$, 87 mmol) and oleic acid (90%, Sigma-Aldrich, 150 mL, 0.48 mol) was prepared in 1L 2-necked round-bottom flask equipped with a reflux condenser. The reaction mixture was heated to 330 ^oC (~15 ^oC min^{-1}) in a heating mantle with magnetic stirring under N_2 blanket (N_2 was blown at the flow rate of 100 mL min^{-1}). After 30 min, oleylamine (0.48mol) was subsequently added into the solution. After 1~2 h from amine addition, black (Fe_3O_4) or green (CoO) precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added excess ethanol.

Usage of dioctylamine in the synthesis of MnO nanoparticles

A mixture of bulk Mn precursor ($MnCO_3$, 87 mmol) and oleic acid (90%, Sigma-Aldrich, 150 mL, 0.48 mol) was prepared in 1L 2-necked round-bottom flask equipped with a reflux condenser. The reaction mixture was heated to 330 ^oC (~15 ^oC min^{-1}) in a heating mantle with magnetic stirring under N_2 blanket (N_2 was blown at the flow rate of 100 mL min^{-1}). The solution gradually became transparent due to the decomposition of $MnCO_3$ over the reaction period of 30 min. Dioctylamine (0.48 mol) was subsequently added into the solution, and the solution colour became green due to the formation of MnO nanoparticles. After 20 min of heating at 330 ^oC, brown precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added excess ethanol.

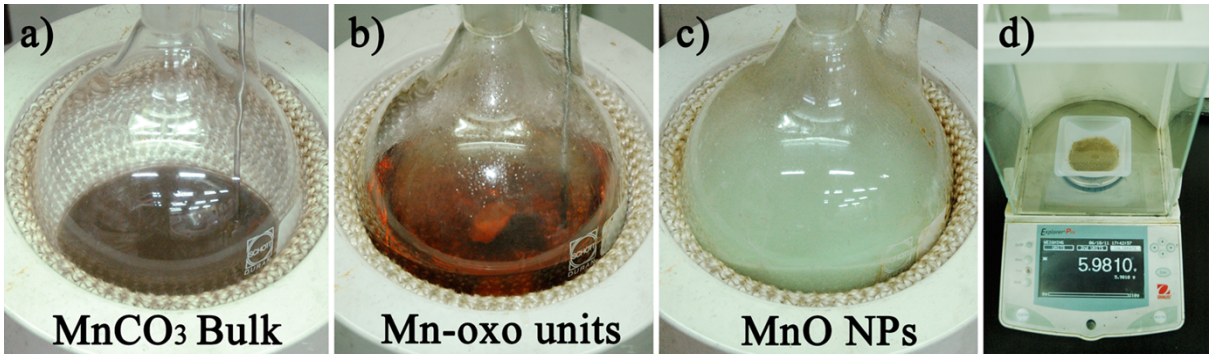

Fig.S1 Scalable synthesis of MnO nanocrystals from bulk $MnCO_3$. a) before reaction, b) after CO_2 release from $MnCO_3$, c) after formation of MnO nanoparticles with added amine, d) multi-gram scale product. 5.98 g of oleic acid stabilized MnO nanoparticles were obtained from 400 mL of solvent. When we tested the nanoparticle formation at twice higher concentration, namely 10.0 g of $MnCO_3$ in 200 mL solvent volume, MnO nanoparticles with the same size and shapes were obtained. Therefore, the ratio of TOA/oleic acid is more important than the sheer solvent volume. But, at this level, it was difficult to visually identify the reaction procession due to the high opaqueness of the reaction mixture. It appears though that the concentration of the reaction mixture can be further increased to meet the requirement of industrial scale production.

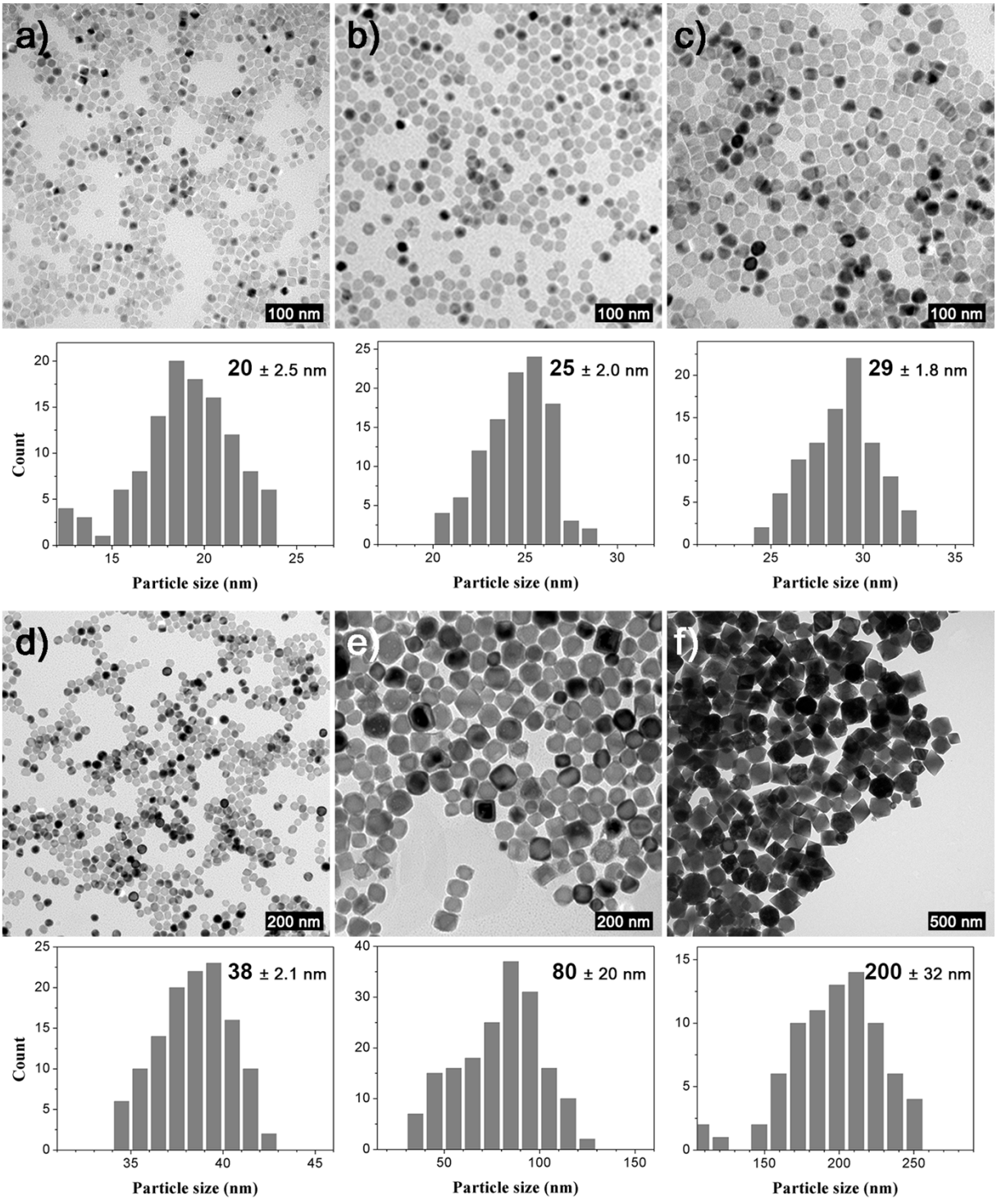

Fig. S2. TEM images and the corresponding histograms for particle size distributions of MnO nanoparticles in Fig. 3: (a) 20 ± 2.5 nm, (b) 25 ± 2.0 nm, (a) 29 ± 1.8 nm, (a) 38 ± 2.1 nm, (a) 80 ± 20 nm, (a) 200 ± 32 nm.

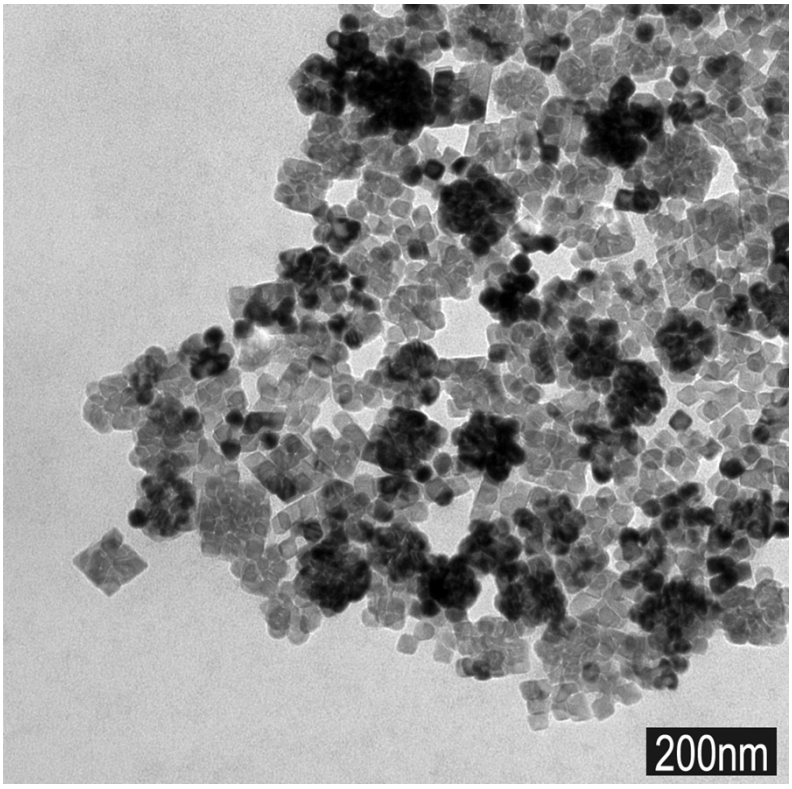

Fig. S3. MnO nanoparticle obtained by using dioctylamine. The obtained MnO nanoparticle size was determined to be 110 nm, which is intermediate of nanoparticle sizes from TOA-only and oleylamine-only conditions. Interestingly, these nanoparticles exhibited multipod morphologies due to surface etching, which results from significant evaporation and loss of dioctylamine from the reaction mixture at high temperature and thereby elevated oleic acid proportion in the reaction mixture.