Supporting information

Shape Evolution of Single-crystalline Mn_2O_3 Using a Solvothermal Approach

Wei-Na Li,[†] Lichun Zhang,[†] Shanthakumar Sithambaram,[‡] Jikang Yuan,[†] Xiong-Fei Shen,[†] Mark Aindow,[†] and Steven L. Suib [†,‡,*]

[†] *Department of Chemical, Materials, & Biomolecular Engineering, and*
[‡] *Department of Chemistry*
55 North Eagleville Rd.,
University of Connecticut, Storrs, CT 06269 (USA)
** Corresponding author. E-mail: steven.suib@uconn.edu*

A typical synthesis was as follows: 4 mmol of $Mn(NO_3)_2$ was dissolved in 13 mL of an organic solvent followed by a vigorous stirring at room temperature for half an hour in a Teflon liner with a volume of 23 mL. Then the Teflon liner was transferred and sealed in an autoclave for heat treatment at 120 ^oC for 20 hours. A variety of different solvents were used to investigate the effect of solvents on the morphology of the resultant Mn_2O_3. In order to investigate the development of Mn_2O_3 crystals, the reactions were also conducted at different temperatures from 100 ^oC to 180 ^oC for 20 hours and at times from 1.5 hours to 20 hours at 120 ^oC, all using ethanol as the solvent.

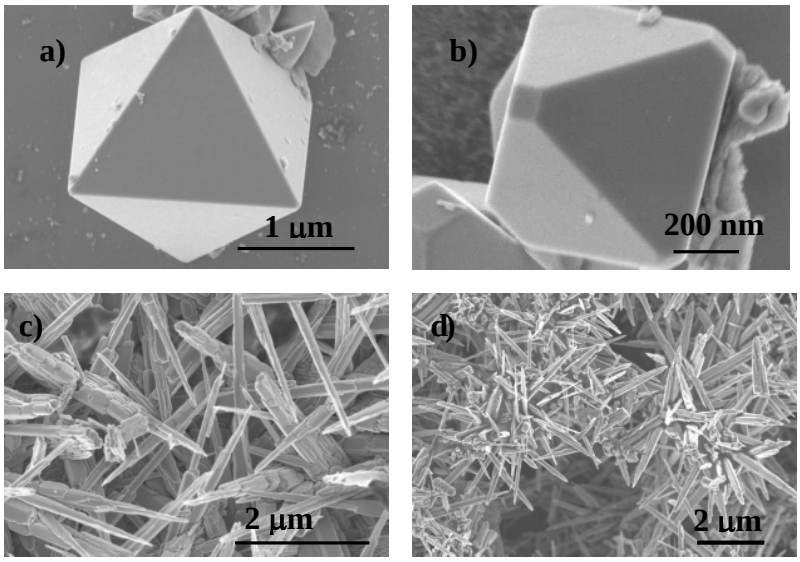

Figure 1. FESEM images of products synthesized in different solvents. a) ethanol, b) 2-butanol, c) benzene, and d) cyclohexane.

Enlarged FESEM pictures of the samples prepared in ethanol and 2-butanol are indicated in Figures 1a and 1b, respectively. The Mn_2O_3 materials obtained in ethanol showed octahedral shapes (Figure 1a), while truncated-octahedral Mn_2O_3 was observed using 2-butanol as solvent. When benzene and cyclohexane were applied in the system, rod-like γ-MnO_2 was observed as indicated in Figures 1c and 1d. The formation of γ-

MnO_2 instead of Mn_2O_3 materials may be due to the lack of –OH groups as reducing agents in benzene and cyclohexane.

Mn_2O_3 octahedra can be formed over a range of temperatures from 100 ^oC to 160 ^oC without a significant change in morphology and crystallinity. However, when the temperature was increased to 180 ^oC, a mixture of bixbyite-c and γ- Mn_2O_3 was produced with rough surfaces of octahedra (Figure 2e). Bixbyite-c octahedra thus cannot be stable up to 180 ^oC.

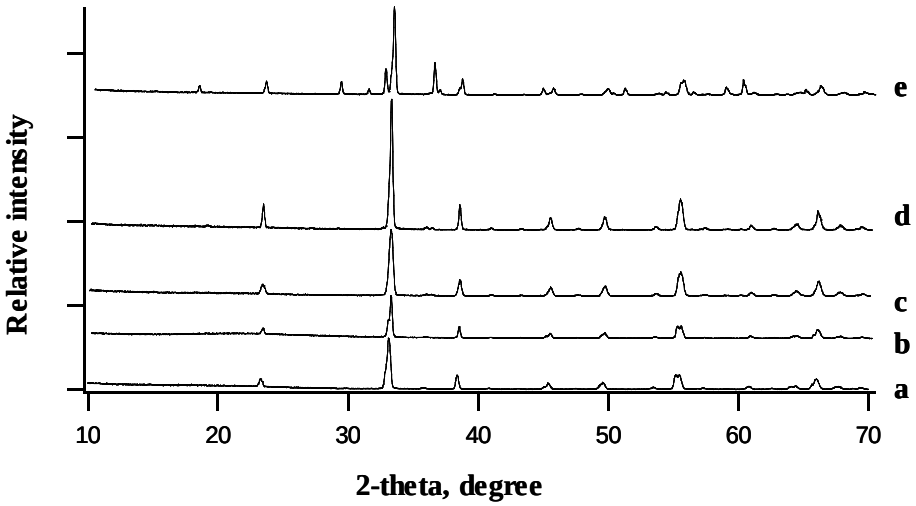

Figure 2. XRD patterns for the samples prepared at different temperatures. (a) 100 ^oC, (b) 120 ^oC, (c) 140 ^oC, (d) 160 ^oC, and (e) 180 ^oC.

Compared with Mn_2O_3 synthesized in various solvents, Mn_2O_3 samples under different reaction temperatures exhibit octahedral habits with similar diameters of 200 nm – 4 μm as shown in Figure 3. However, the octahedra obtained at 100 ^oC formed aggregates, while the samples prepared at 120 ^oC, 140 ^oC, and 160 ^oC exhibit both aggregates and single octahedra. Unlike the octahedra prepared at relatively low temperatures of 100 ^oC

to 160 ^{o}C, the samples prepared at 180 ^{o}C indicate octahedra with very rough and bumped surfaces and broken octahedra as well (Figure 3e).

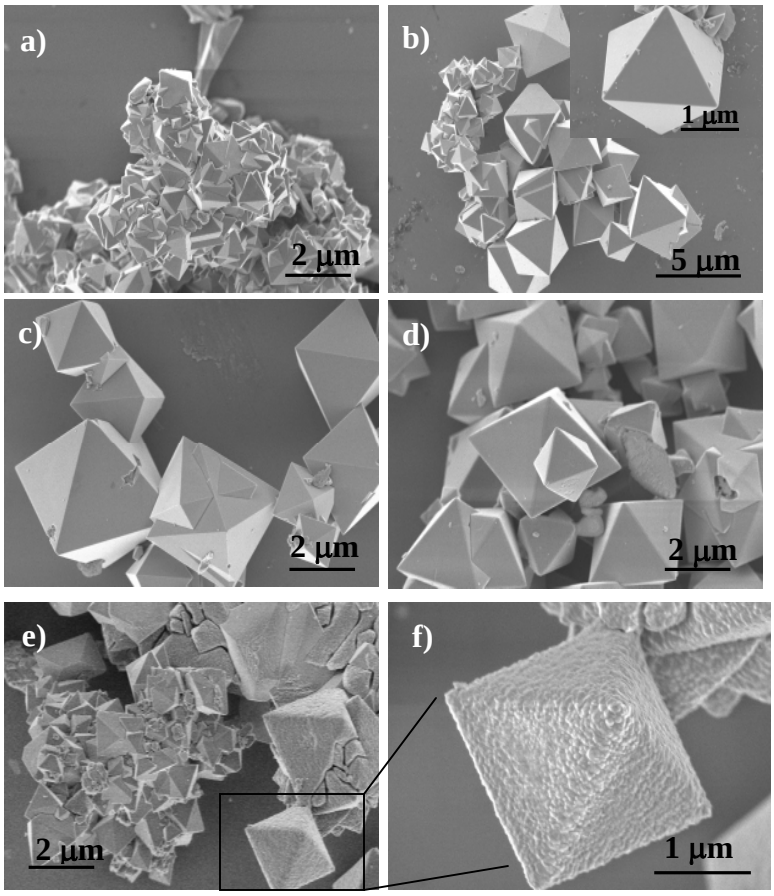

Figure 3. FESEM images of products synthesized under different reaction temperatures: a) 100 ^{o}C, b) 120 ^{o}C, c) 140 ^{o}C, d) 160 ^{o}C, and e) 180 ^{o}C, f) an enlarged image of typical octahedron synthesized at 180 ^{o}C.