Electronic Supplemental Information for

Solid state microwave synthesis of highly crystalline ordered mesoporous hausmannite Mn₃O₄ films

Yanfeng Xia,^a Zhe Qiang,^b Byeongdu Lee,^c Matthew L. Becker,^a and Bryan D. Vogt^{b,*}

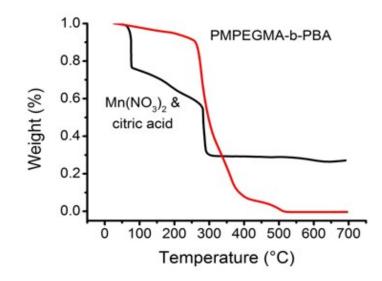


Figure S1. TGA traces for complex of manganese nitrate-citric acid (black) and PMPEGMA-PBA (red). The decomposition onsets of manganese nitrate-citric acid curve correspond to carbonate and oxide formation.

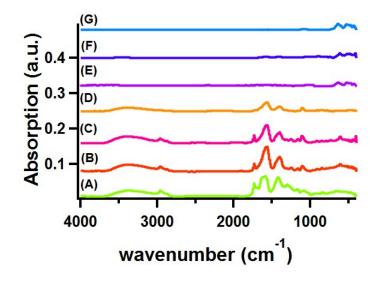


Figure S2. FT-IR spectrum of (A) as-cast film of PMPEG-PBA micelle templated manganese nitratecitric acid complex film (B) manganese carbonate film with template remaining on conventional heating at 200°C for 1 h (C) manganese carbonate/oxide film on conventional heating at 200°C for 1 h and microwave heating at 10 W for 30 s (D) manganese carbonate/oxide film on conventional heating at 200°C for 1 h and microwave heating at 30 W for 5 s (E) manganese carbonate/oxide film on conventional heating at 200°C for 1 h and microwave heating at 50 W for 5 s (F) manganese oxide film on conventional heating at 200°C for 1 h and at 300°C for 30 min (G) manganese oxide film on conventional heating at 200°C for 1 h and microwave heating at 50 W for 30 s.

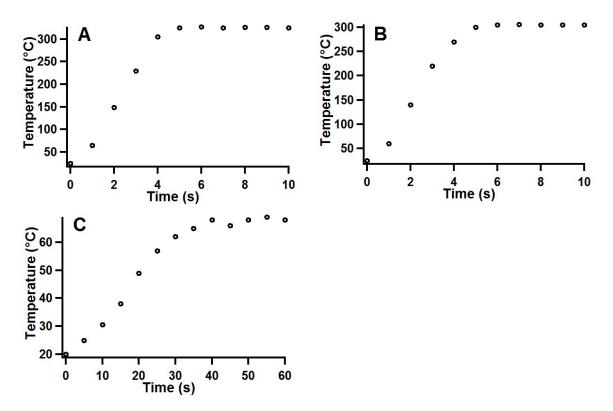


Figure S3. Influence of microwave time at 50 W on the apparent surface temperature of (A) manganese oxide film (fabricated by prior heating at 300°C for 30 min) on Si wafer, (B) blank Si wafer as a control, and (C) manganese oxide film (fabricated by prior heating at 300°C for 30 min) on quartz. Without the manganese oxide, there is much smaller change in the temperature for the quartz compared to Si substrate.

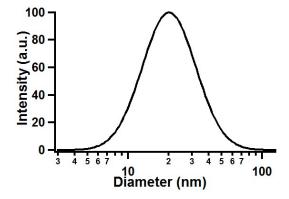


Figure S4. Dynamic light scattering size distribution for the block copolymer template in the THF/Ethanol mixture solvent.

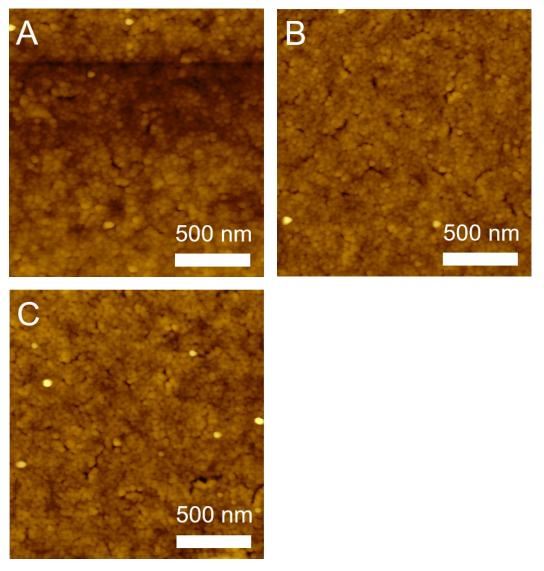


Figure S5. The AFM micrographs of (A) manganese oxide film on Si wafer by conventional heating at 200°C for 1 h and at 280°C for 30 min (B) manganese oxide film on Si wafer by conventional heating at 200°C for 1 h and at 320°C for 30 min (C) manganese oxide film on Si wafer by conventional heating at 150°C for three days, 200°C for 1 h and at 300°C for 30 min

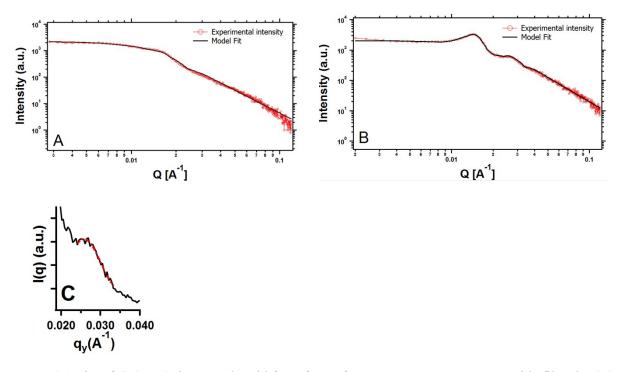


Figure S6. Fits of GISAXS data to spheroid form factor for mesoporous manganese oxide films by (A) conventional heating and (B) microwave and (C) A zoom-in GISAXS figure of microwave treated sample showing the secondary peak position by Gaussian fit. (Black solid line for raw data and red dash line for Gaussian fit)

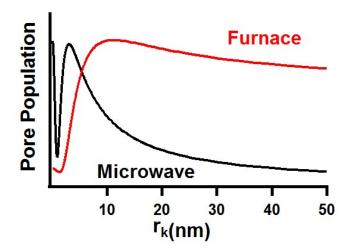


Figure S7. Pore population obtained from the EP adsorption isotherm for microwave treated (black) and furnace treated (red) manganese oxide films.

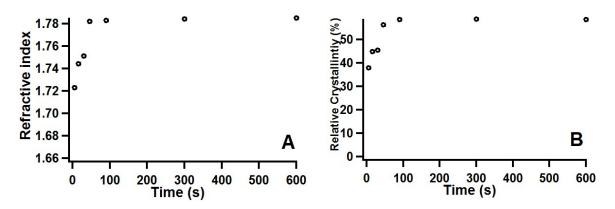


Figure S8. (A) Evolution in the refractive index of manganese oxide film as a function of microwave heating time at 50W. (B) Crystallinity change estimated using Bruggman Effective Medium Approximation (BEMA) model of manganese oxide film on conventional heating at 200°C for 1 h and microwave heating at 50W for 5s, 15s, 30s, 45s, 90s, 300s and 600s.

The calculation of crystallinity is done by two steps. The first step is to calculate the refractive index of the non-porous Mn_3O_4 using Bruggman Effective Medium Approximation (BEMA) model with the two components of air and Mn_3O_4 . The second step is to calculate the crystallinity of Mn_3O_4 by determining the percentage of crystal part and amorphous part from BEMA model again. For example, for the sample that undergoes 45 s microwave treatment, the porosity is 12.4% and the refractive index of the Mn_3O_4 can be calculated to be 1.895. Then the percentage of the crystal part can be calculated by applying BEMA model again.

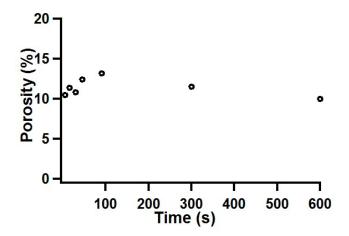


Figure S9. Estimated porosity for manganese oxide films as a function of microwave heating time at 50W.