

Crystalline Mesoporous $K_{2-x}Mn_8O_{16}$ and ϵ - MnO_2 by Mild Transformations of Amorphous Mesoporous Manganese Oxides and Their Enhanced Redox Properties.

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SUPPORTING INFORMATION

Experimental:

a) Chemicals:

Manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, $\geq 97.0\%$), 1-butanol (anhydrous, 99.8%), block-poly(ethylene glycol)-block-Poly(propylene glycol)-block-Poly(ethylene glycol) PEO₂₀-PPO₇₀-PEO₂₀ (Pluronic P123), potassium chloride (KCl, $\geq 99.0\%$), manganese (III) oxide (Mn_2O_3 , 99%), and manganese (II, III) oxide (Mn_3O_4 , 97%) were purchased from Sigma-Aldrich. Concentrated sulfuric acid (H_2SO_4 , 95-98%) and concentrated nitric acid (HNO_3 , 68%-70%) were purchased from J. T. Baker. All chemicals were used as received without any purification.

b) Synthesis of Mesoporous Manganese Oxides:

Amorphous mesoporous manganese oxide was synthesized using the procedure of Poyraz et al.² and used as the precursor for the synthesis of several other mesoporous manganese oxide materials with different crystal structures. In a typical synthesis, 5.0 g (0.02 mol) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in a solution containing 14 g (0.188 mol) of 1-butanol, 2 g (0.032 mol) of HNO_3 and 2 g (3.44×10^{-4} mol) of P123 surfactant in a 150 ml beaker at room temperature (RT) and under magnetic stirring. The obtained clear gel is placed in an oven at 120°C for 4 h. The obtained powder was washed several times with ethanol and then the powder is centrifuged. Finally, the powder is dried in a vacuum oven overnight. The dried powder was subjected to a heating cycle [150°C for 10 - 12 h + 250°C (3 h) + 350°C (2 h)]. The powder was removed from the oven and naturally cooled down to RT after each heating step. All heat treatments were done under air. The sample is labelled as Meso-Mn-A, where A stands for amorphous.

Synthesis of Mesoporous Mn_2O_3 :

Amorphous Meso-Mn-A sample was heated at 450°C (1 h) to obtain crystalline mesoporous Mn_2O_3 material. The sample was labelled as Meso- Mn_2O_3 . Commercial Mn_2O_3 (purchased from Sigma-Aldrich) is labeled as C- Mn_2O_3 .

Synthesis of Mesoporous ϵ - MnO_2 :

Amorphous Meso-Mn-A sample (0.3 g) was dispersed in 50 mL 0.5M H_2SO_4 aqueous solution (DDI water) and sonicated at RT for 10 min. The formed homogeneous suspension was transferred to a glass autoclave and the autoclave was placed in an oven running at 70°C for 2 h. The obtained powder was filtered and washed several times with DDI water and finally dried in a vacuum oven over night. The sample is labelled as Meso- ϵ - MnO_2 .

Synthesis of Mesoporous $K_{2-x}Mn_8O_{16}$ (Cryptomelane) (OMS-2):

Amorphous Meso-Mn-A sample (0.3 g) was dispersed in a 50 mL aqueous solution (DDI water) containing 0.5 M H_2SO_4 + 0.5 M KCl and sonicated at RT for 10 min. The formed homogeneous suspension was transferred to a glass autoclave and the autoclave was placed in an oven running at 70°C for 2 h. The obtained powder was filtered and washed several times with DDI water and finally dried in a vacuum oven overnight. The sample is labelled as Meso-OMS-2. A non-porous OMS-2 material was also synthesized for comparison with reflux methods using the procedure of Iyer et al.¹⁷. OMS-2 material synthesized with reflux methods is labeled as R-OMS-2.

c) Catalyst Characterization:

PXRD analyses were performed on a Rigaku Ultima IV diffractometer (Cu $K\alpha$ radiation of 1.5406 Å) with an operating voltage of 40 kV and a current of 44 mA. The Both low-angle ($2\theta = 0.5 - 8$) and wide-angle ($2\theta = 10 - 75$) diffraction patterns were collected. N_2 sorption isotherms were collected on a Quantachrome Autosorb-1-1C automated adsorption system. The samples were degassed at 200°C for 4 h prior to the analyses. The surface areas were calculated using Brunauer-Emmett-Teller (BET) method and the pore size distributions were obtained by the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms. HR-TEM images of synthesized mesoporous materials were recorded on a JEOL 2010 FasTEM microscope operating at 200 kV. Temperature programmed reduction mass spectrometry (TPR-MS) was completed using an MKS PPT Quadrupole Residual Gas Analyzer equipped with a vacuum manifold that allows for the sampling of gas streams at or near atmospheric pressure. A 100-mg powder sample was loaded into a quartz tube and placed inside a programmable tube furnace. Prior to analysis, the sample was treated at 150°C in air for one hour and brought back to room temperature. A feed gas composed of 5% H_2 in He gas was flowed at 500 sscm while the temperature was ramped at a rate of 10°C/min from room temperature to 800°C.

d) CO Oxidation:

The CO oxidation reactions with O₂ were performed on a continuous flow fixed bed quartz tubular reactor at atmospheric pressure. For each test, 100 mg of catalyst was packed in a quartz tube and the catalyst surfaces were cleaned at 200°C for 1 h under helium flow (15 cc/min). After cooling down the catalysts under ambient conditions to RT, a gas mixture containing 1% CO, 2% O₂ balanced in N₂ was passed through the catalyst bed at a flow rate of 20 mL/min. The outlet gas streams were analyzed by an online gas chromatograph (SRI 8610C Multiple Gas Analyzer #1 GC) equipped with a thermal conductivity detector (TCD). The reaction temperature was measured using a K-type thermocouple inserted directly into the catalyst bed. The reaction conversions were calculated using CO, O₂, and CO₂ concentrations; N₂ was used as an internal standard.

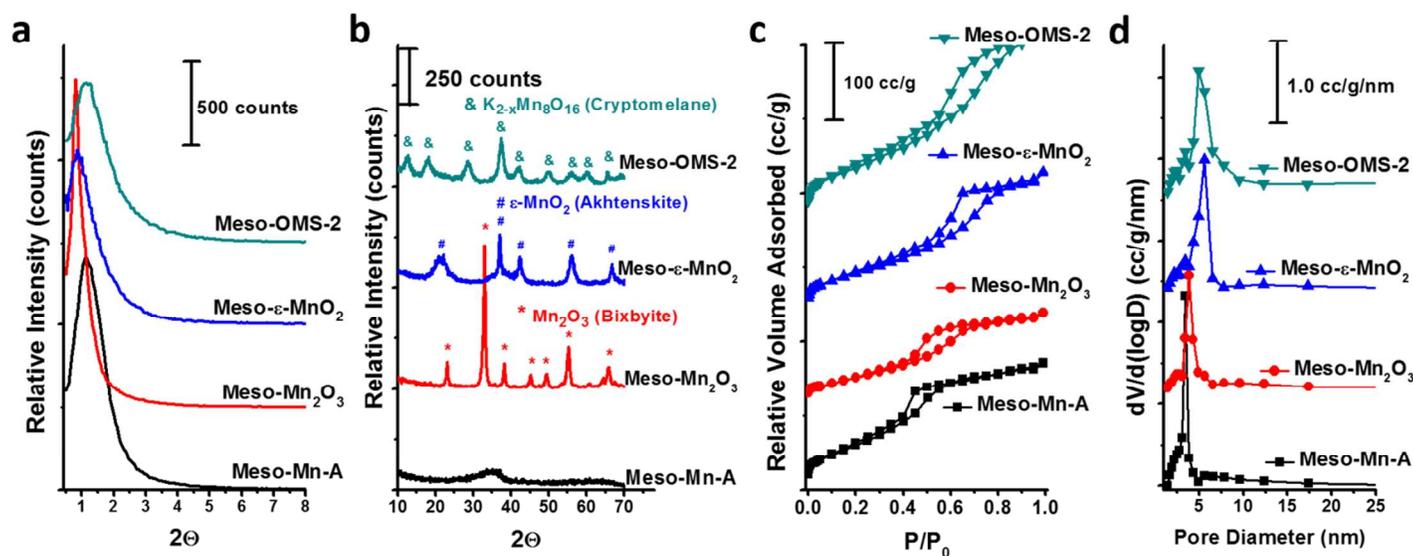


Figure S1. (a) Low-angle PXRD, (b) wide-angle PXRD, (c) N_2 sorption isotherms, and (d) BJH Desorption pore size distributions of mesoporous manganese oxides: Meso-Mn-A, Meso-Mn₂O₃, Meso- ϵ -MnO₂, and Meso-OMS-2.

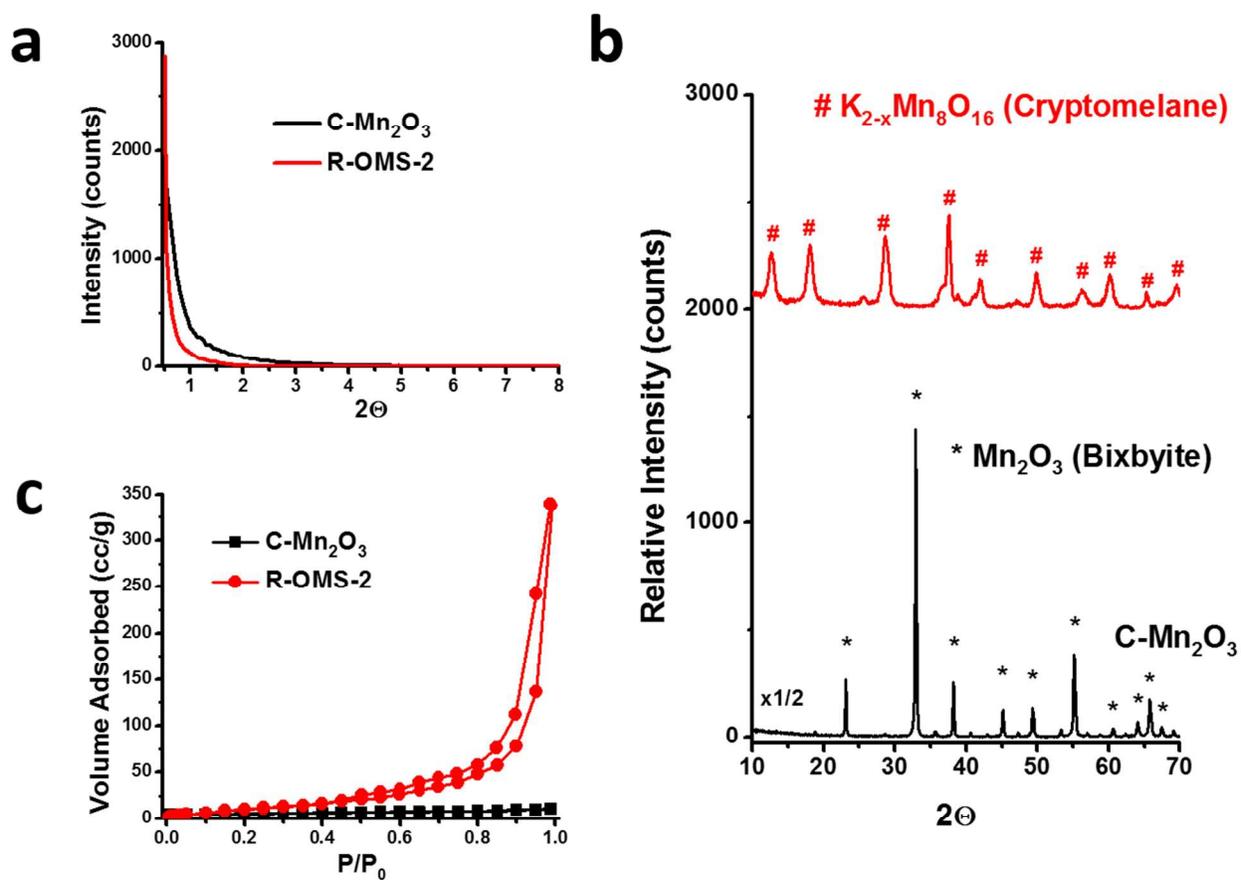


Figure S2. (a) Low-angle PXRD, (b) wide-angle PXRD, (c) N₂ sorption isotherms of C-Mn₂O₃ and R-OMS-2 samples.

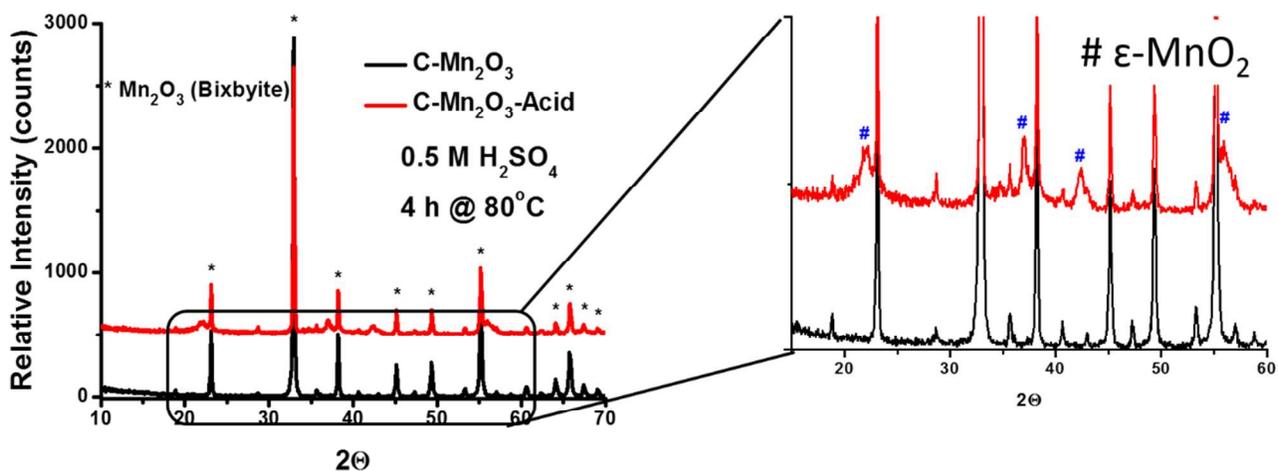


Figure S3. PXRD patterns of commercial Mn_2O_3 (C- Mn_2O_3) and acid treated commercial Mn_2O_3 (C- Mn_2O_3 -Acid). C- Mn_2O_3 was kept in 0.5 M H_2SO_4 for 4 h @ 80°C . The black box was enlarged in the inset.

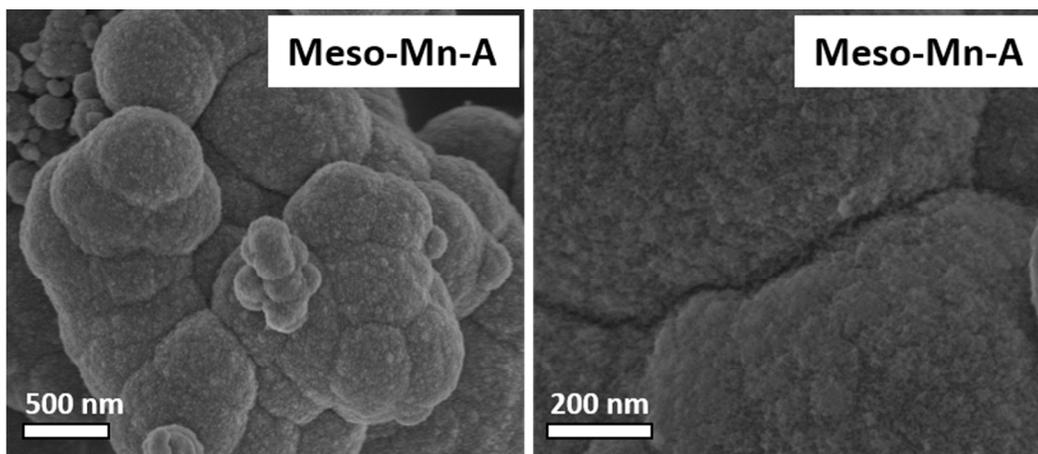


Figure S4. SEM images of mesoporous amorphous manganese oxide (Meso-Mn-A) sample.

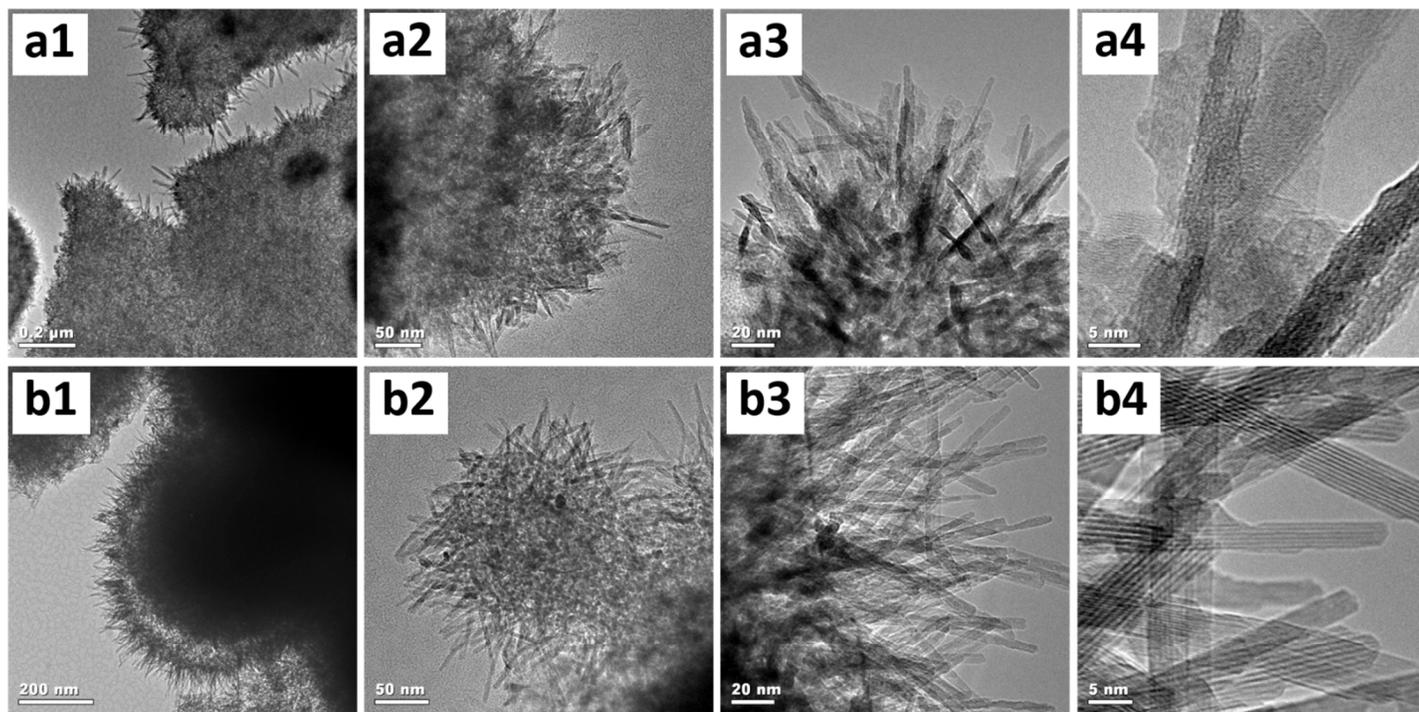


Figure S5. HR-TEM images of mesoporous manganese oxides. (a1-4) Meso- ϵ - MnO_2 and (b1-4) Meso-OMS-2. The scale bars are 200 nm (a1 & b1), 50 nm (a2 & b2), 20 nm (a3 & b3), and 5 nm (a4 & b4).

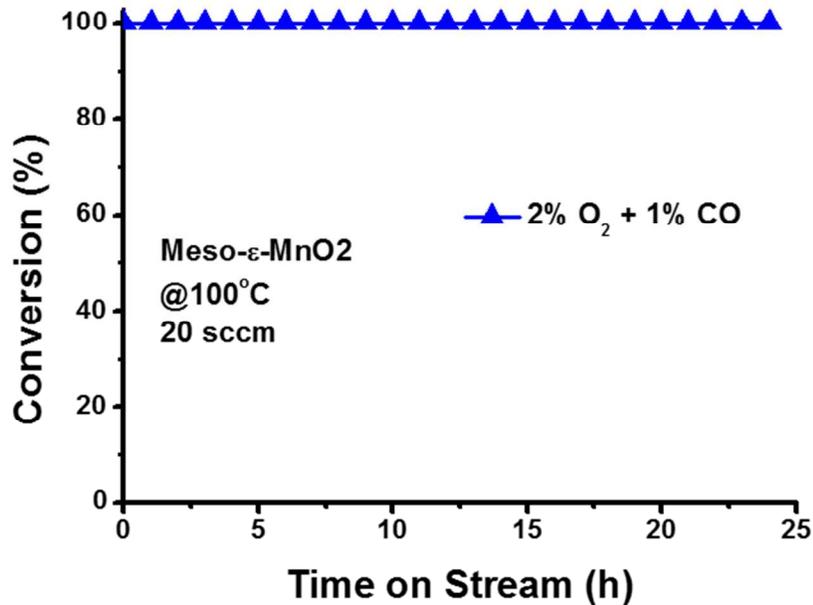


Figure S6. Catalytic stability test of Meso- ϵ -MnO₂ sample for catalytic oxidation of CO. 2% O₂ + 1%CO (balanced in N₂) at 100°C for 24 h (the flow rate is 20 sccm).

Equation S1: Dissolution of Mn₂O₃.



Equation S2: disproportionation.



Equation S3: overall (Equation S1 + Equation S2)



Equation S4: CO Oxidation on Manganese Oxide Surfaces

