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Supporting Information

Efficient electrochemical water oxidation catalysis by nano-structured Mn_2O_3

A. Singh,*[a] D. Roy Chowdhury, [b] S. S. Amritphale,[a] N. Chandra [a], I.B. Singh,[a]

[a] *Advance Material and Process Research Institute, Bhopal, India*

[b] *Indian Institute of Science Education and Research Center, Bhopal, India*

Experimental Section:

Materials: Reagent or analytical grade chemicals were used as received from commercial suppliers unless stated otherwise. Deionized water was used throughout. The sodium hydroxide electrolyte (1 M NaOH) was prepared by dissolving appropriate amount of sodium hydroxide in deionized water.

Synthesis of Manganese Oxide: The synthesis of β-MnO_2 was carried out under hydrothermal conditions following a literature procedure.[20] Nanostructured MnOOH was synthesized by hydrothermal oxidation of Mn^{2+} by $S_2O_8^{2-}$ at pH 10. 8 mM $MnSO_4$ and 8 mM $(NH_4)_2S_2O_8$ were dissolved separately in distilled water and then mixed slowly at pH 10. pH was maintained using lithium hydroxide. The mixture was then heated at 130^{o}c for ten hours in Teflon lined autoclave. The precipitates obtained were filtered and washed thoroughly using distilled water and dried in air. After that the precipitate was dried at 300^{o}c for 3 hours to get MnO_2 and at 600^{o}C for one hour to get Mn_2O_3. For synthesis of C-Mn_2O_3, commercial MnO_2 purchased from sigma Aldrich was annealed at 600^{o}C for one hour.

Characterization: The morphology of the MnO_x films were analyzed using NOVEN nano scanning electron microscope (SEM). The crystal structure was investigated using Miniflex II desktop X-ray diffractometer and the diffraction pattern was scanned in steps of 0.020 ° (θ) between 20° and 60°. Surface area was measured using BELSORP MAX (BEL Japan) volumetric adsorption analyzer. XPS measurements were performed using Thermo Scientific Model: MULTILAB 2000 Base system.

Electrode Preparation: The electrodes for electrochemical characterization were prepared by pasting a mixture of manganese oxides, activated charcoal and PVDF (75:15:10) using propylene carbonate as solvent on ITO electrode area of 0.25 cm^2. Followed by pasting the material on ITO, the electrodes were kept at room temperature for half an hour and then at 100^{o}C for one hour. Amount of material pasted on ITO electrodes were calculated by weighing the ITO glass before and after pasting material using microbalance. The films were then transferred in three electrode electro-chemical cell with 1 M NaOH electrolyte, Ag/AgCl as reference electrode and Pt sheet as counter electrode. Linear scan voltammogram was recorded at scan rate of 5 mV/sec. A 365 nm LED, with λ bandwidth 5 nm and output power of 5 mW/cm^2 was used as light source.

Electrochemistry: All electrochemical experiments were performed at 22^{o}C in a three-electrode cell connected to an Solatron potentiostat. The reference electrode was a CHI Ag/AgCl (3 M NaCl) glass bodied electrode, which has a potential of 0.200 V vs. NHE. Pt foil was used as counter electrode. Indium doped tin oxide (ITO) films were used as working electrodes. The sodium hydroxide solution (1 M NaOH) was used as electrolytes. All potentials are specified with reference to Ag/AgCl. The potentials reported throughout this article were not corrected for the uncompensated resistance between the reference and working electrodes. Current has been reposted on the basis of ITO geometric area throughout the article. For difference percentage volume of water experiment, LSV were recorded by increasing the amount of 1 M NaOH electrolyte to the 0.1 M $TBAPF_6$ in acetonitrile.

Table S1: Mn $2p_{3/2}$ spectral fitting parameters for L-Mn_2O_3 sample.

Multiplet no.	**Position (eV)**	**%**
1	640.2	13.9
2	641.3	46.3
3	642.6	15.3
4	643.5	12.1
5	644.4	7.1
6	645.5	5.1

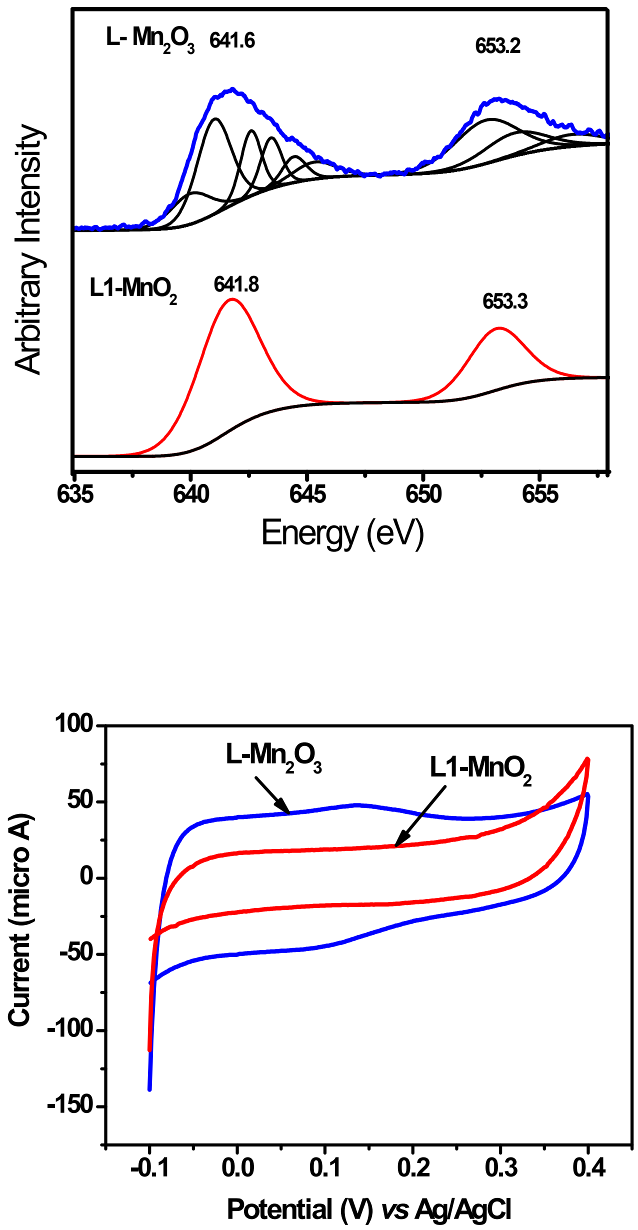

Fig. S1: Mn 2p spectra recorded for the L-Mn_2O_3 and L-MnO_2 samples (top). CV recorded for the L1-MnO2 and L-Mn2O3 films in 1M NaOH electrolyte at scan rate of 5 mV/sec (bottom).

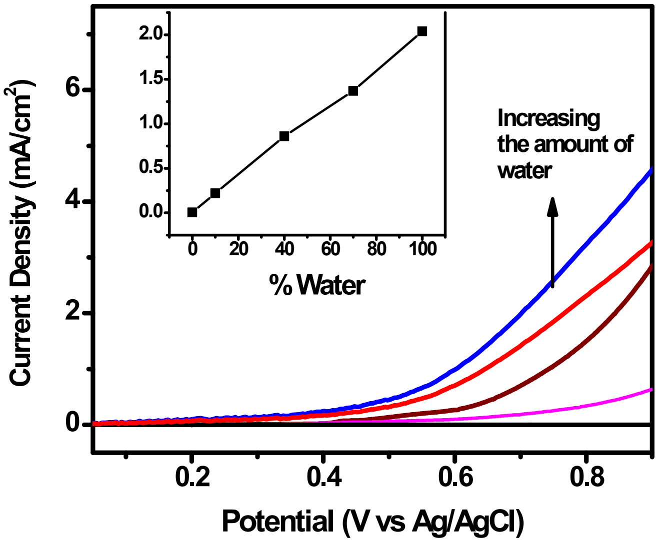

Fig. S2: LSV as a function of increasing water content (% v/v), in acetonitrile (0.1 M Bu4NPF6). Inset displays plot of current obtained at 0.7 V *vs* Ag/AgCl for different volume percentage of water in acetonitrile.

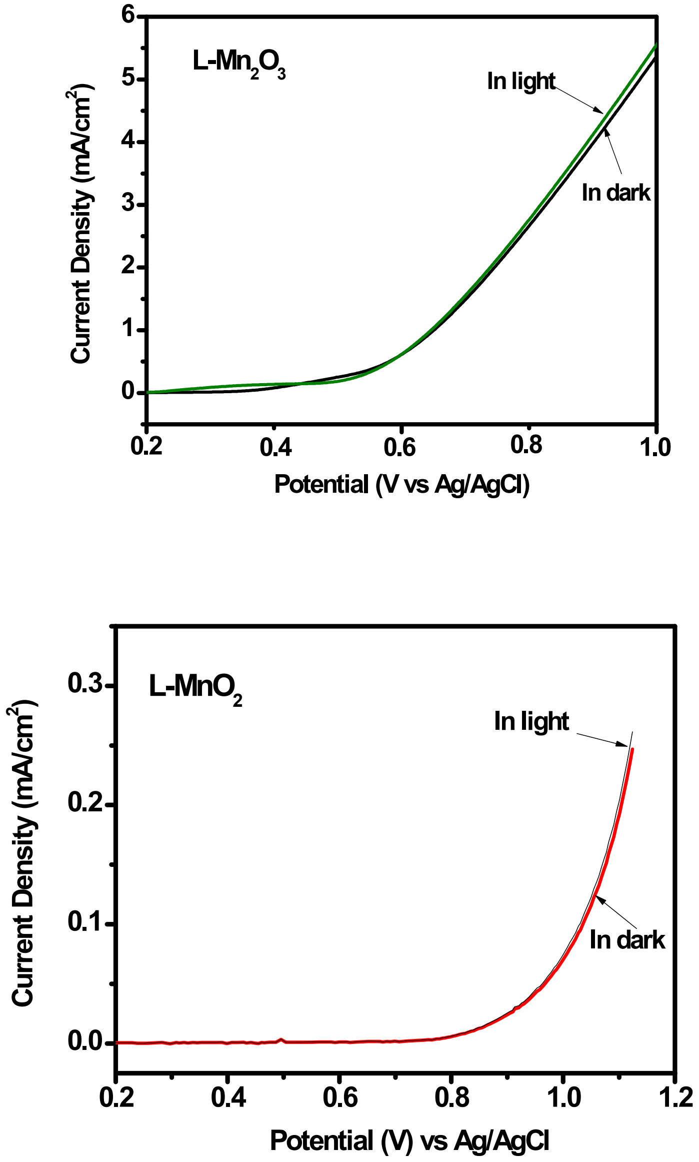

Fig. S3: LSV of L-Mn_2O_3 and L-MnO_2 recorded in 1M NaOH at scan rate of 5 mV/sec in presence and absence of light.

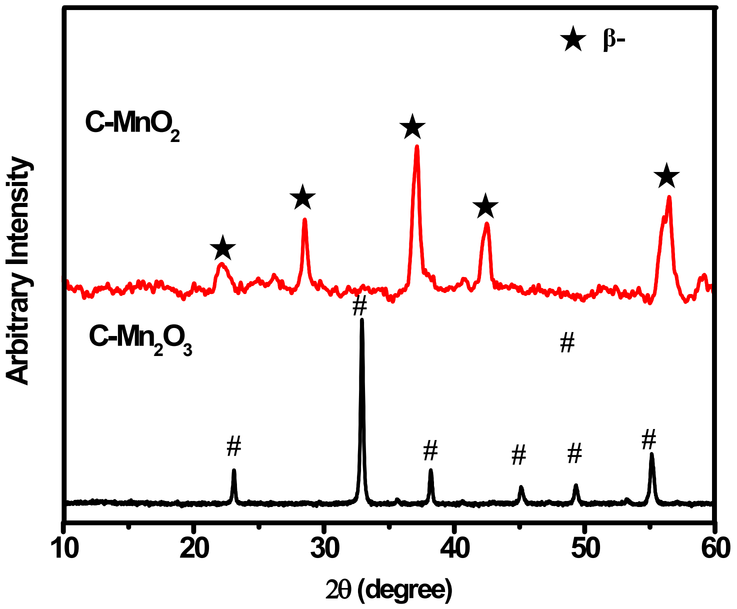

Fig. S4: PXRD patterns obtained for C-MnO_2 and C-Mn_2O_3.where ★ refers to the peaks corresponding to the β-MnO_2 phase, and # refers to the peak corresponding to pure Mn_2O_3 phase.

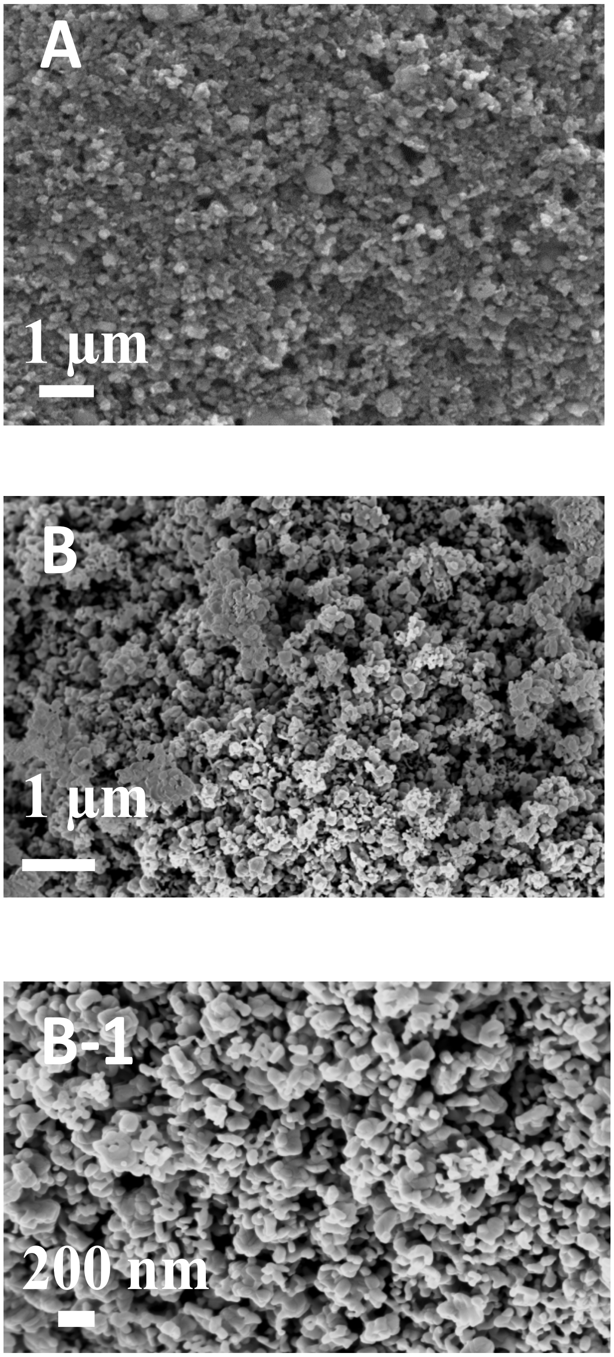

Fig. S5: Low magnification SEM images of the C-MnO_2 (A), low and high magnification image of C-Mn_2O_3 (B, B-1).

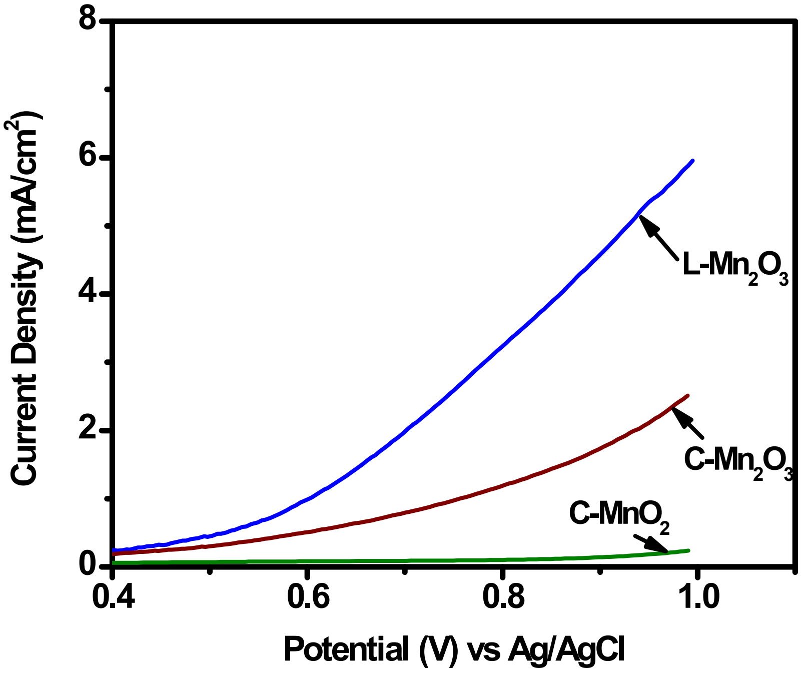

Fig. S6: LSV of L-Mn_2O_3, C-Mn_2O_3 and C-MnO_2 recorded in 1M NaOH at scan rate of 5 mV/sec.