Supporting Information for:

Highly Active β-Manganese Oxide Electrocatalysts for Water Oxidation

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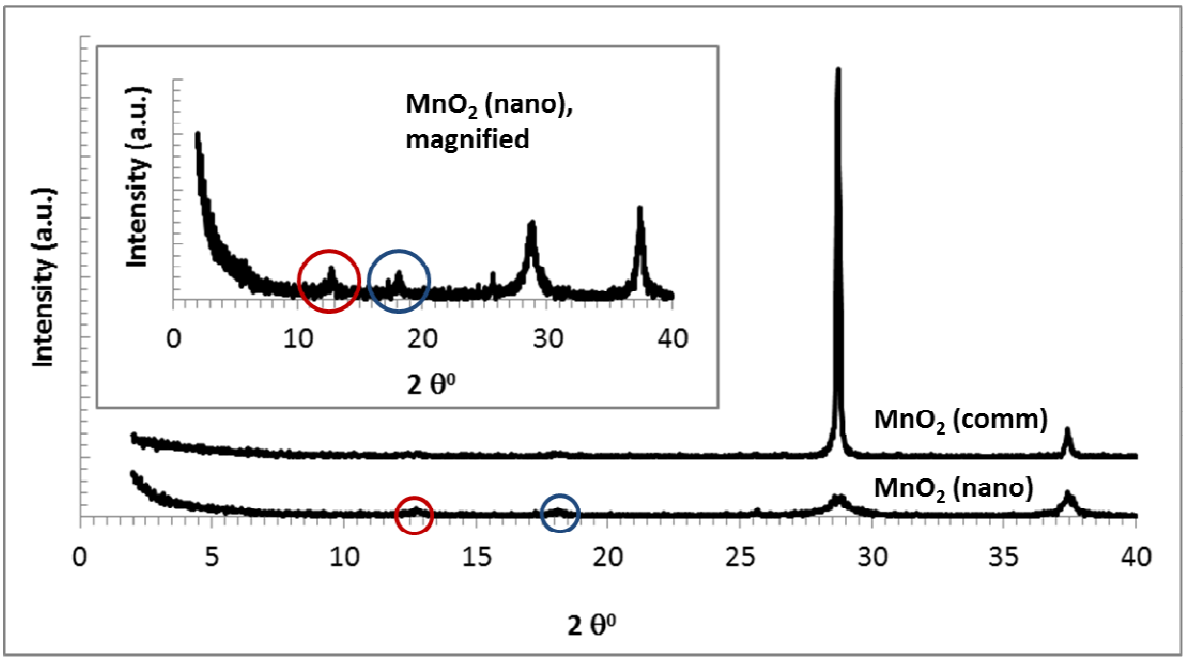

Fig.S1. Low angle XRD patterns of MnO_2 (comm) and MnO_2 (nano) after screen-printing. The inset shows a magnified image of the MnO_2 (nano) pattern. The circles show the peaks observed below 20°, which could indicate the presence of non-pyrolusitye phases (red circle: 12.5, tentatively assigned to birnessite, blue circle: 18°, tentatively assigned to hausmannite.). However, the other characteristic peaks of birnessite or hausmannite were not observed in the XRD pattern.

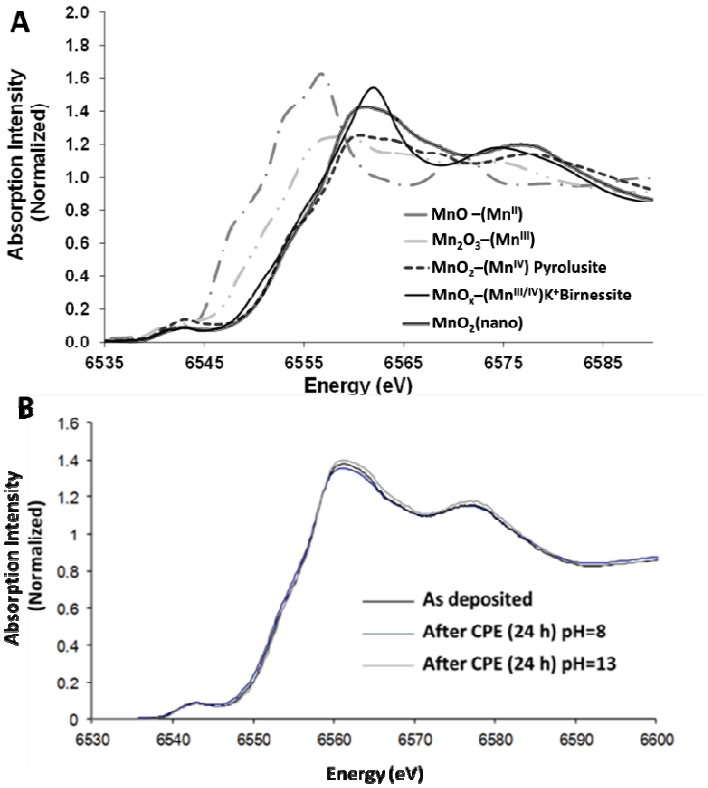

Fig.S2. A. XAS spectra of the "as deposited MnO_x material compared to references MnO, Mn_2O_3, Mn_3O_4 , K^+ Birnessite and Pyrolusite. B. XAS spectra of the MnO_2 (nano) films. Black trace: freshly printed film; blue trace: after 24 hours of CPE in a pH 8 electrolyte (0.10 M Na_2SO_4 adjusted to pH with NaOH), η = 490 mV; grey trace: after 24 hours of CPE in a pH 13 electrolyte (0.10 M NaOH).

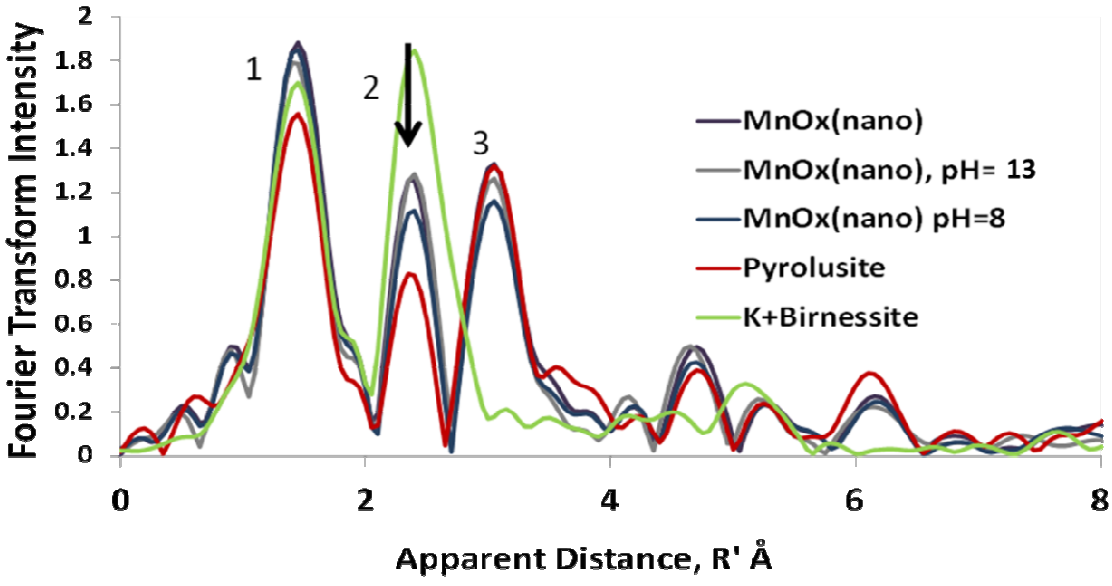

Fig.S3: Fourier Transform of the EXAFS of MnO_x (nano) films. The data are substantially affected by the matrix of the electrode and are scaled by 0.7 to facilitate comparison to transmission Pyrolusite (red) and K+Birnessite (green) data.

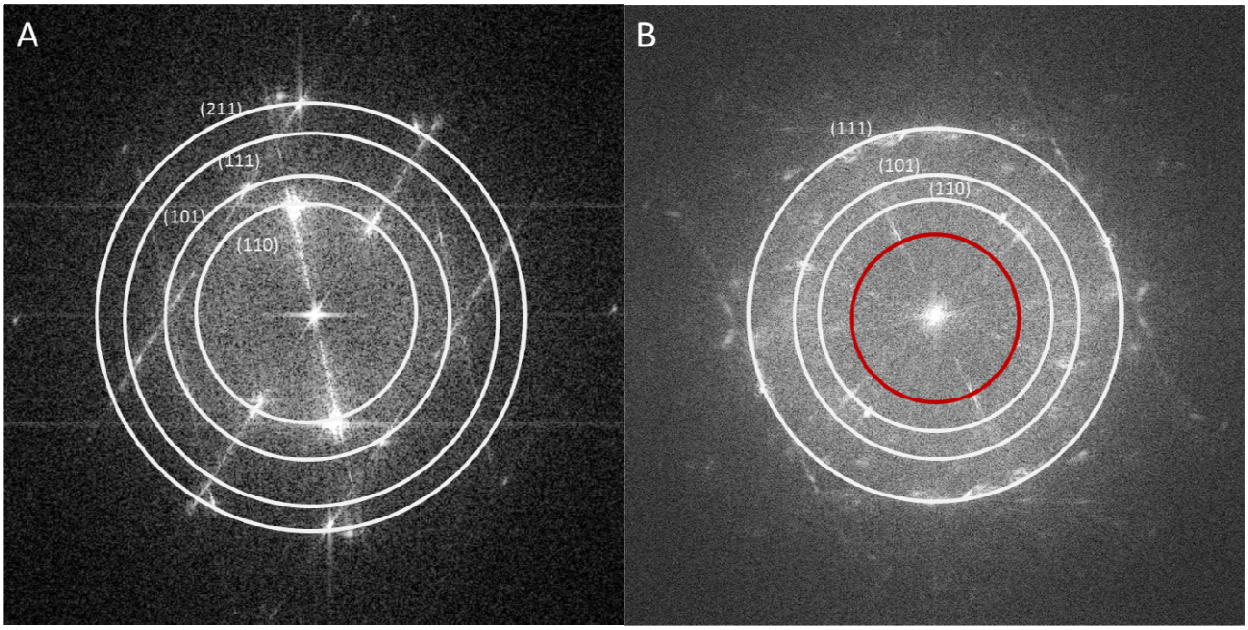

Fig.S4. FFT images of MnO_2 (nano). A: FFT of HRTEM images of nanorods; B: FFT of HRTEM images of nanoparticles. The white circles correspond to the (110), (101), (11) and (211) facets of β-MnO_2. The red circle shown in B corresponds to a lattice spacing of 4.9 Å, indicating the presence of a non-pyrulosite phase.

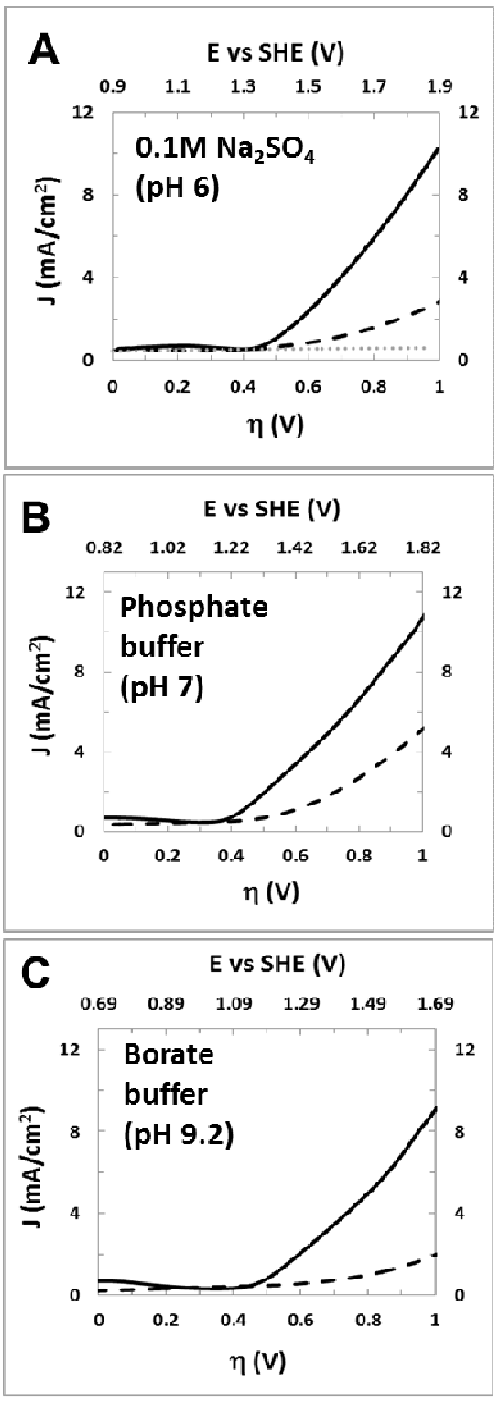

Fig.S5. Linear sweep voltammograms of the two catalyst films in buffer solutions as compared to LSV testing at pH 6. The dashed black trace represents MnO_2 (comm) and the continuous black trace represents MnO_2 (nano). A) pH 6, in a 0.1M Na_2SO_4 electrolyte, B) pH 7, in a phosphate buffer electrolyte, C) pH 9.2 (in a borate buffer). The scan rate was 5 mVs^{-1} and T = 20 ^{0}C in each case.

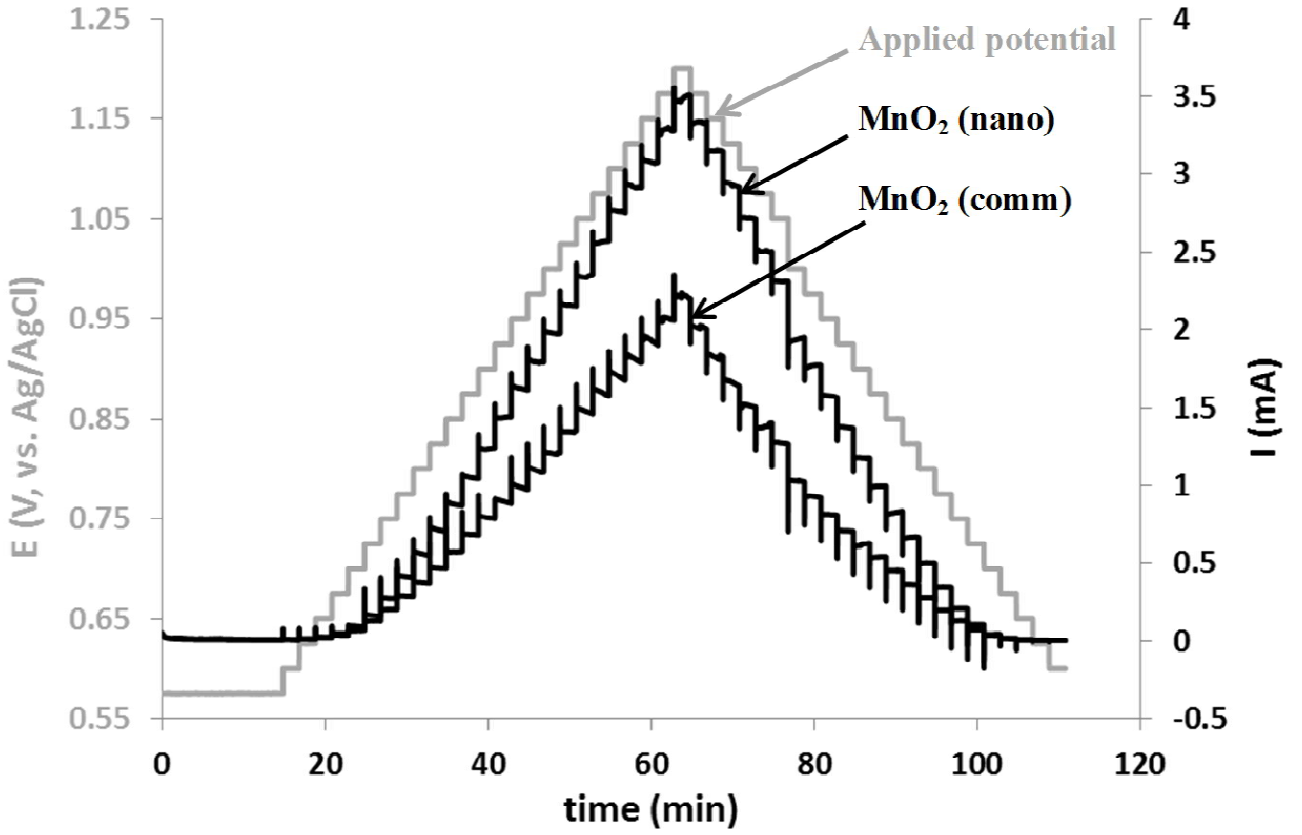

Fig.S6. Tafel plots taken using a staircase voltammetry method. ENREF 34[34] Currents were sampled at the end of each step. Tafel plots were constructed from both the anodic and cathodic scans and the averaged points were presented in Figure 7.

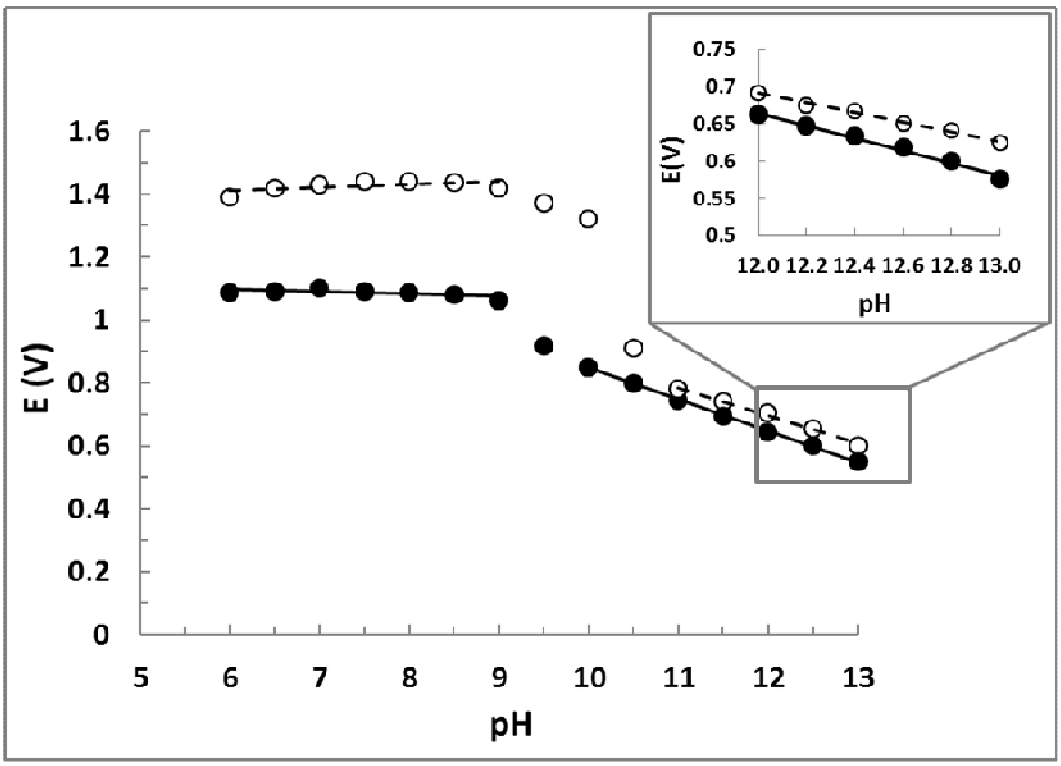

Fig.S7. E-pH relationships for MnO_2 (comm) (ʘ) and MnO_2 (nano) (●) covering the pH 6 -13 range in 0.5 pH increments and in 0.2 pH increments between pH 12.0 and 13.0.

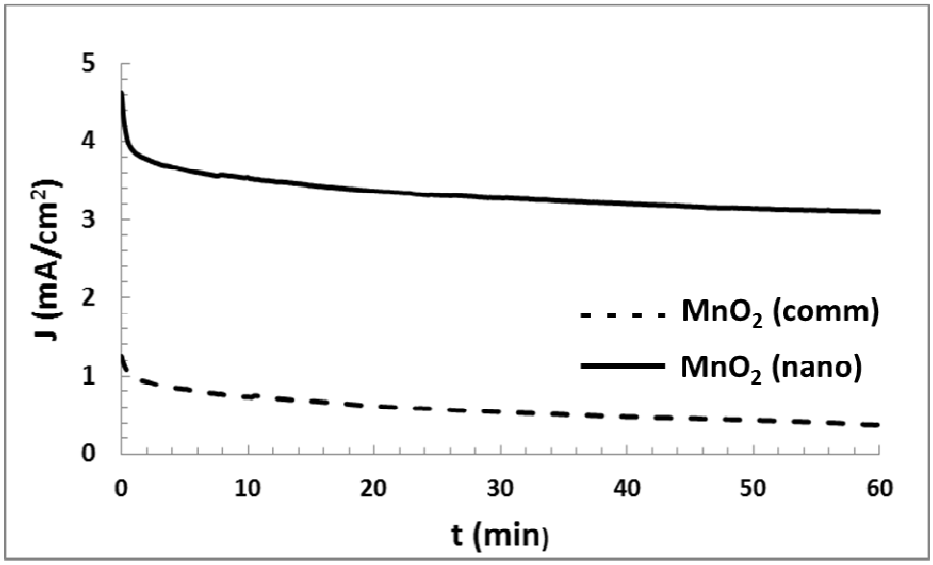

Fig.S8. Controlled potential electrolysis (CPE) measurements of MnO_2 (comm) (dashed trace) and MnO_2 (nano) (solid trace) in a pH 7 phosphate buffer. 1.22 V vs Ag/AgCl (η = 0.6 V) was applied over 60 minutes in each case. T=20°C.