Supporting Information

Nano - size amorphous calcium - manganese oxides as efficient and biomimetic water oxidizing catalysts for artificial photosynthesis: Back to manganese

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Materials and Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1}. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) were added to 1 mL of concentrated nitric acid and H_2O_2, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS.

The temperature of the reactor (a colourless three-neck, round-bottom glass flask (50 ml)) remained constant (25.0 ^{o}C) with a bath and a constant stirring rate was also maintained. Oxygen evolution studies were carried out with a luminescent DO probe oxygen electrode (HQ40d portable dissolved oxygen meter from Hach company). All solutions were prepared using doubly deionized water. All rates were measured at 25.0 ^{o}C using the method of initial rates from at least 100 s.

Water Oxidation Experiment

Oxygen evolution from aqueous solutions in the presence of $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 ^{o}C in the circulating water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, the water in the reactor was replaced with Ce(IV) (40.0 ml, 0.004 - 0.64 M) solution. Without catalyst, Ce(IV) was stable in this condition and oxygen evolution was not observed. After deaeration of Ce(IV) with argon, calcium manganese oxide as several small particles were added and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S1).

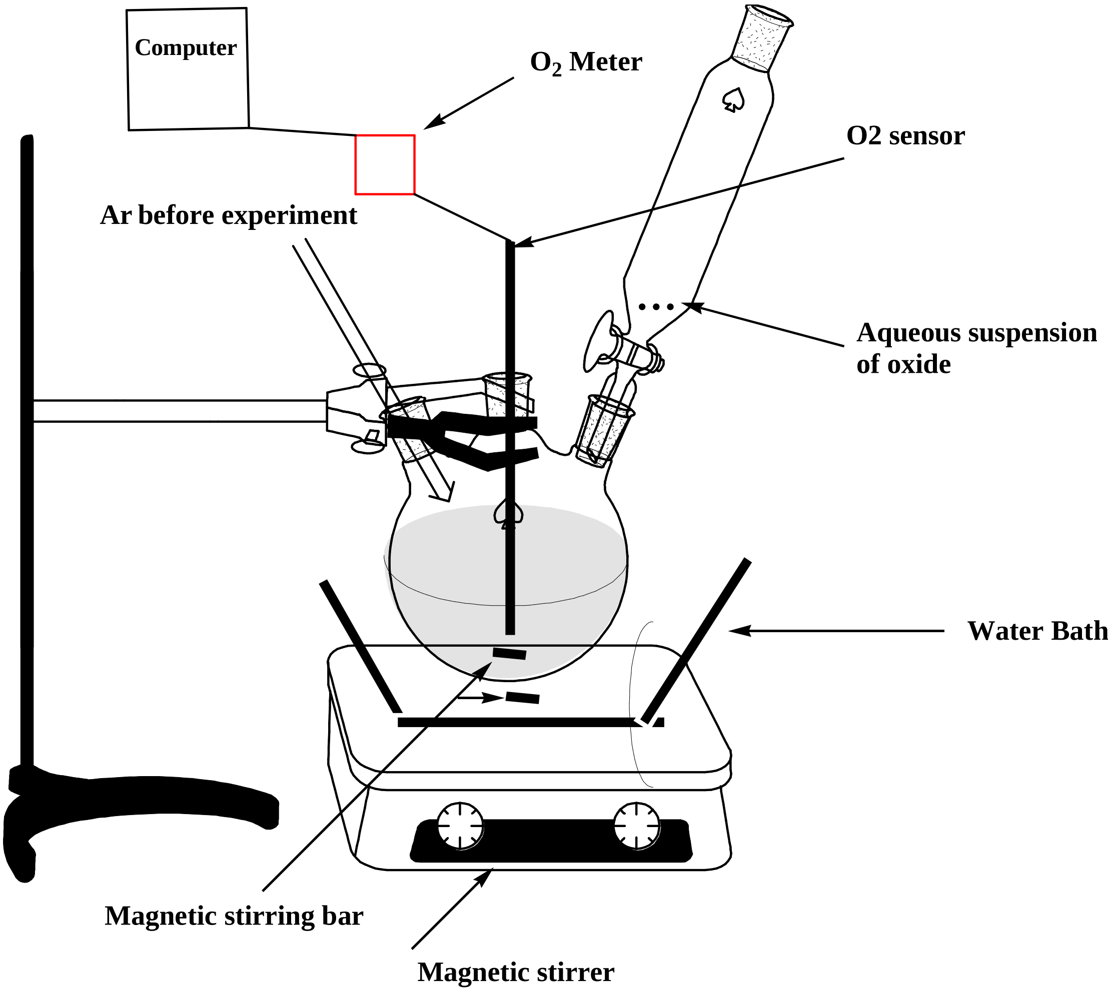
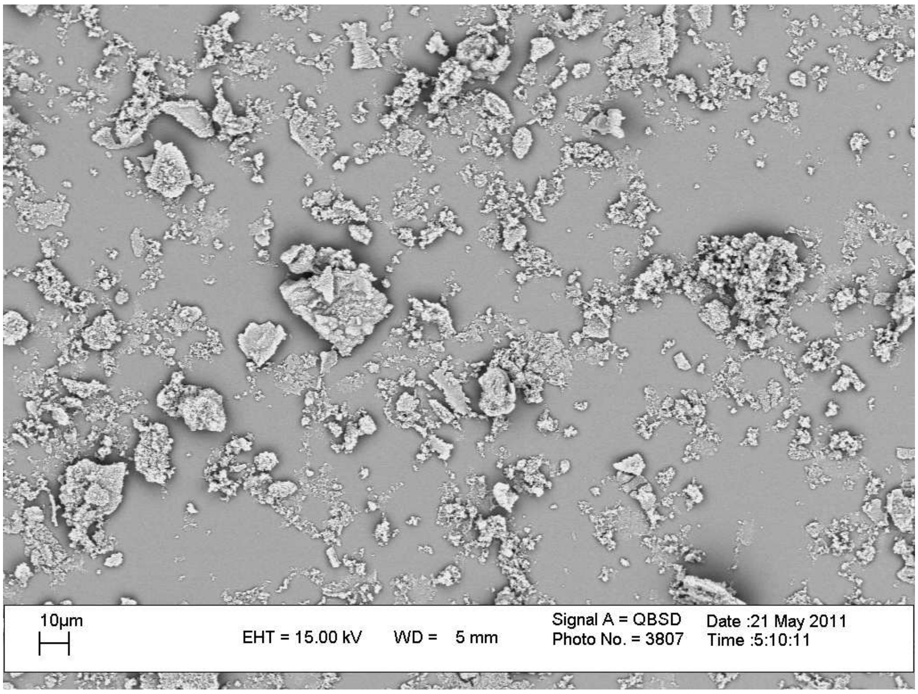


Fig. S1. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence of $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) and manganese calcium oxides.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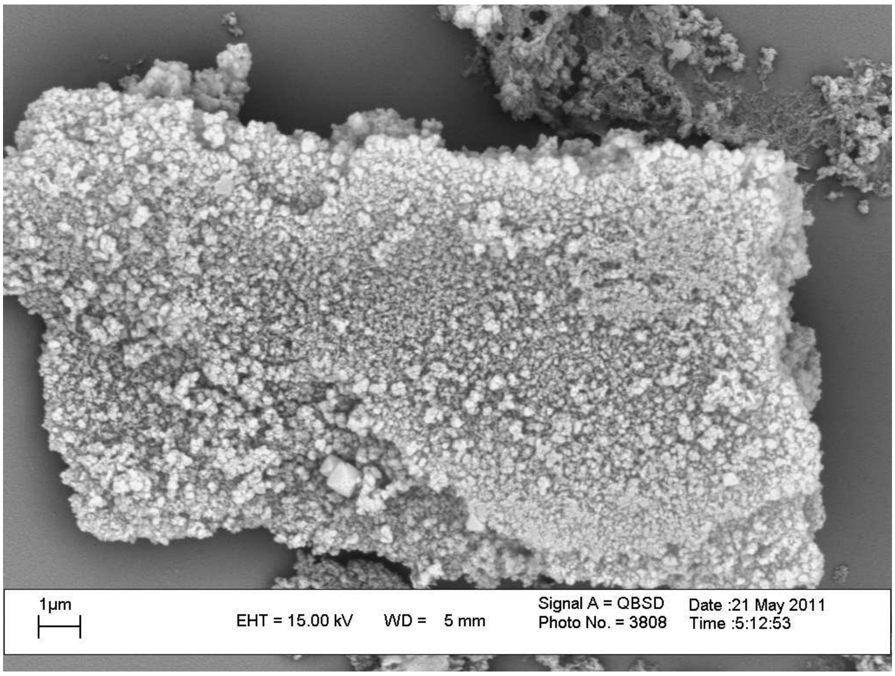
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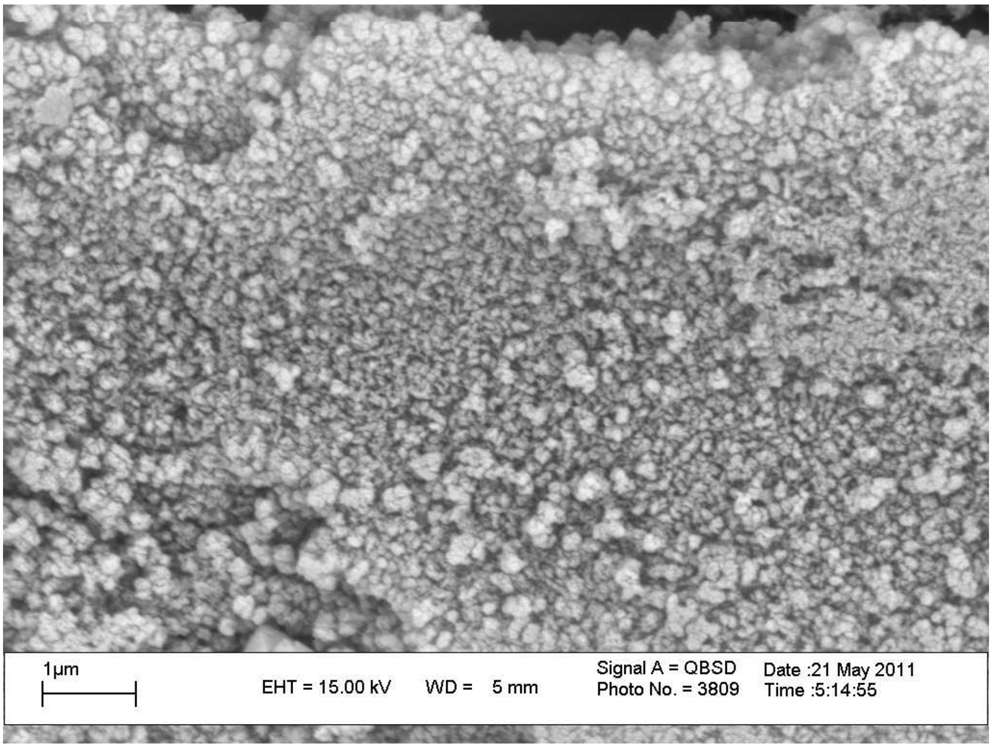
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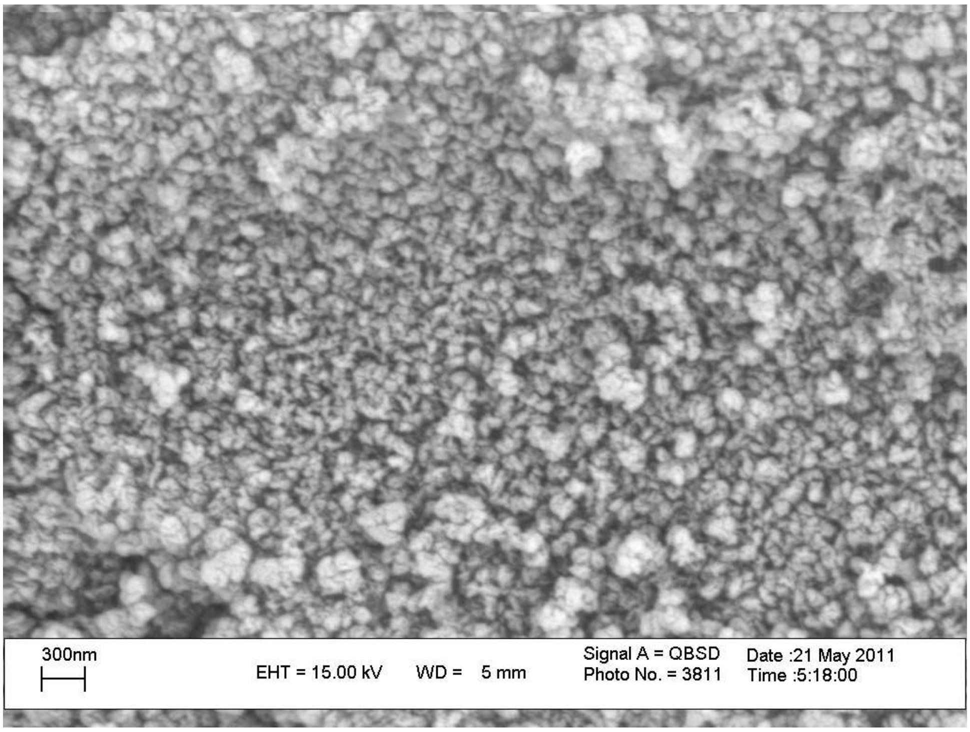
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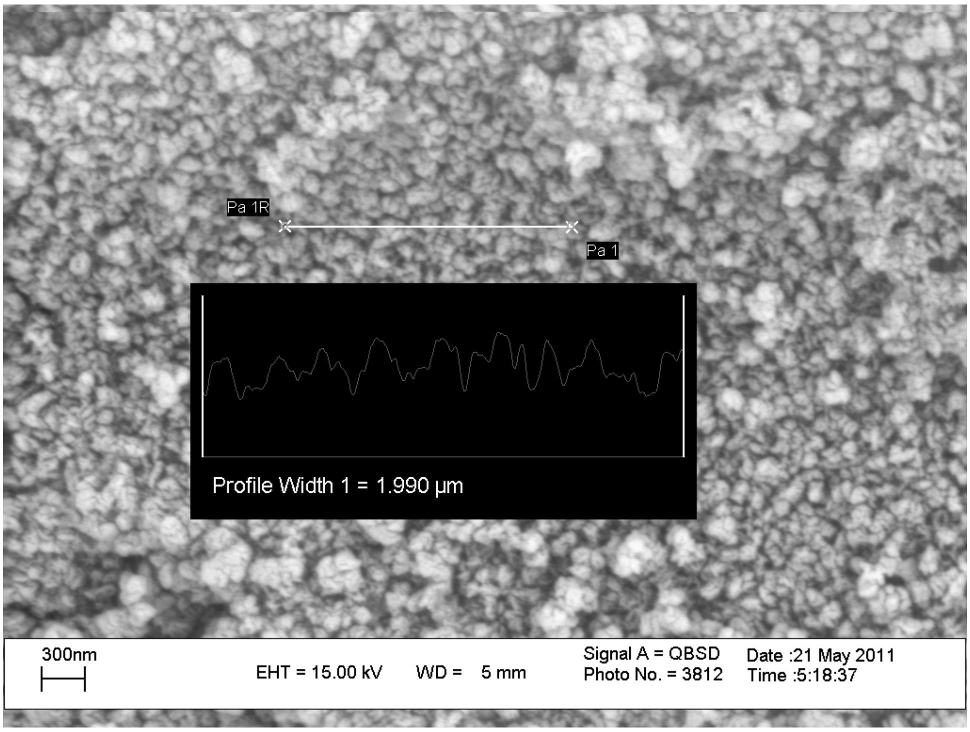
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Pa 1
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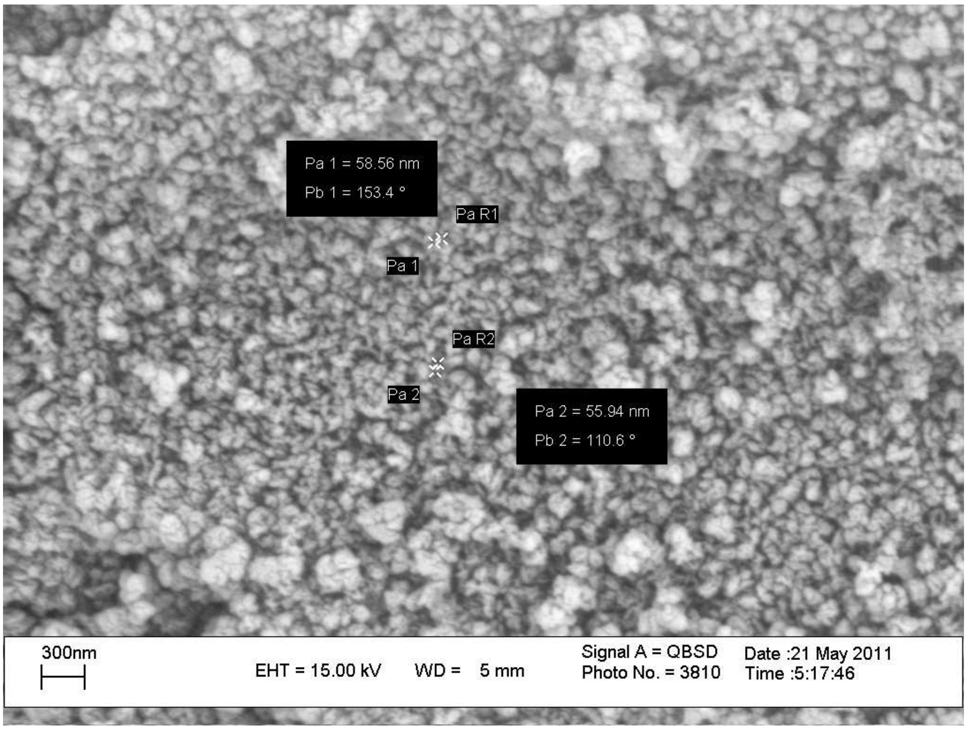
e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Pa R1
Pa 1
Pa R2
Pa 2
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Pb 2 = 110.6 °
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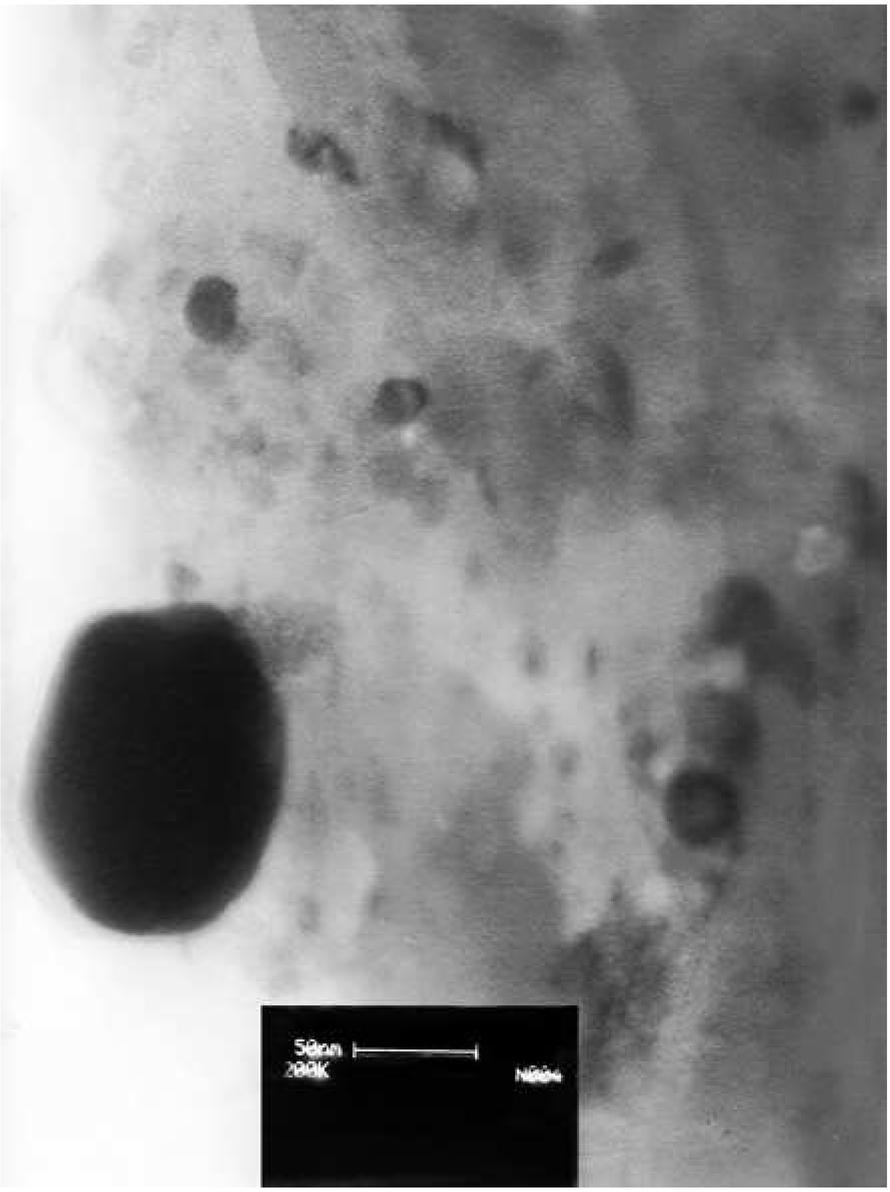
f

g

h

i



j

k

Fig. S2. SEM micrographs of nano size manganese calcium oxide (a-f). TEM images of nano size manganese calcium oxide (g-k).

Synthesis of compound

Different conditions were used to obtain the catalysts for water oxidation but the best catalyst was synthesized using the below condition:

Solution **1**: $Ca(Cl)_2.4H_2O$ (4.0 mmol, 732 mg) and $Mn(CH_3COO)_2.4H_2O$ (5.6 mmol, 1372 mg) were dissolved in water (5 mL). The mixture was stirred for about 10 min. at room temperature.

Solution **2**: to a solution of $KMnO_4$ (2.4 mmol, 379 mg) in 60 mL water, KOH was added to obtain a hot saturated KOH solution.

Addition of solution **1** to solution **2** under vigorous stirring resulted in a dark precipitate. Then the mixture was allowed to cool with continued stirring for 2 h.

The obtained suspension was filtered and washed using distilled water (3L) before being allowed to dry for 12 h at 60°C in an oven. Then the solid was heated to 400°C for 10 h in air to obtain a brown powder. Yield: (~%99); AAS: 47.0%Mn (theor.: 47.2%), 16.9% Ca (theor.: 17.3%); IR (cm^{-1}): 3400 (br, O–H), see Fig. S2 (but there are more bands there at <1000.

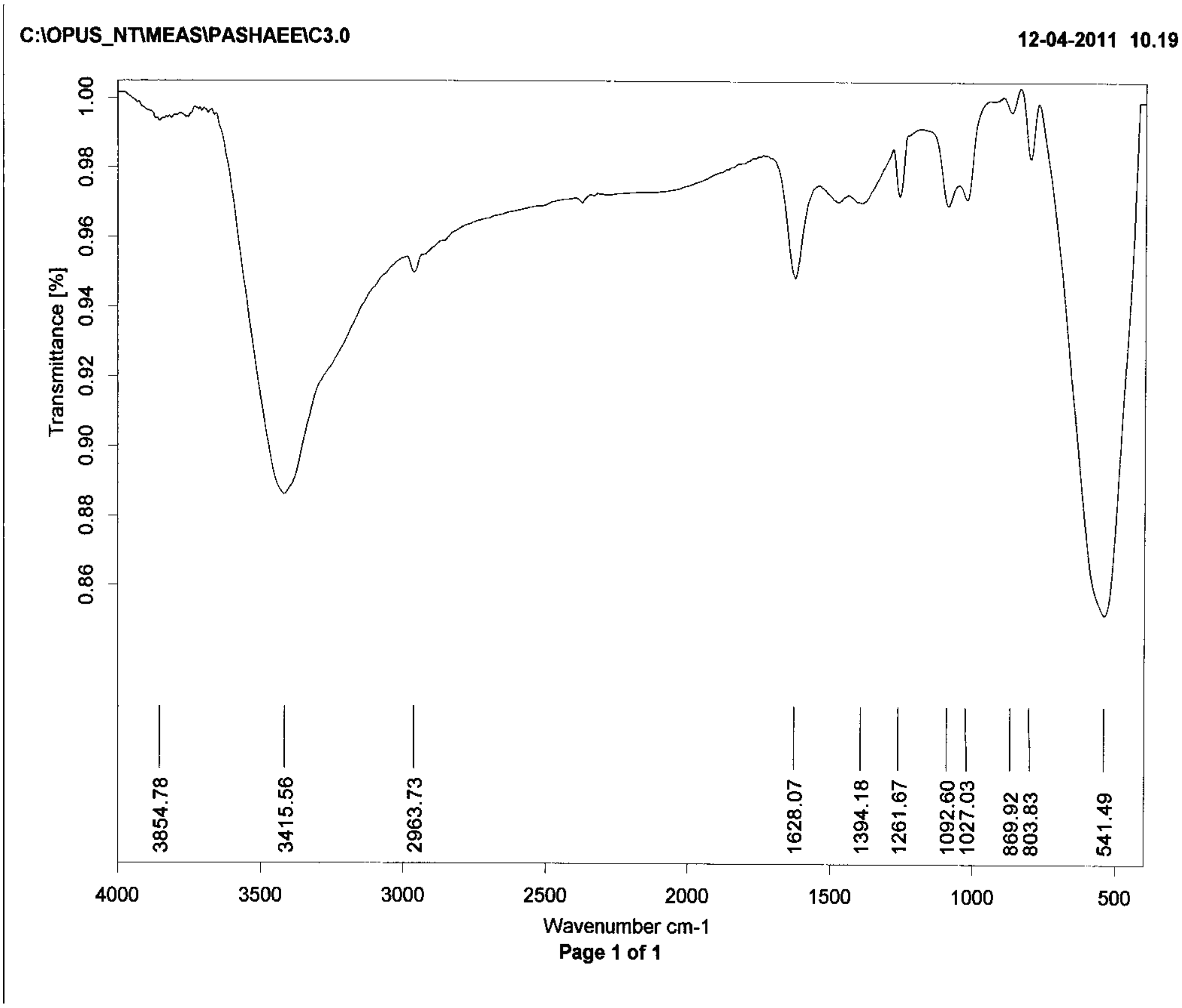


Fig. S2. IR spectrum of the nano – size calcium manganese oxide.

Table1S. Oxygen evolution rates in mmol O_2 per second and mol manganese ion in each manganese compound.

Compound	Oxidant	TOF (mmol$_{O2}$.mol^{-1}$_{Mn}$).s^{-1}	Ref.
$CaMn_2O_4.H_2O$ (Nano particles)	Ce(IV)	2.0	This work
Mntptz	Oxone	0.001	1
$Mn_2O_2(terpy)_2(OH_2)_2$	Ce(IV)	0.05	2
$Mn_4O_4(MeOPh_2PO_2)$/Nafion	Electrochemistry[a]	0.24	3
Manganese Schiff base	Ce(IV)	0.02	4
$[Mn_2(dipic)_2(H_2O)_6].2H_2dipic$[b]	Oxone	0.07	5
MnO_2	Ce(IV)	0.03	6
Mn_2O_3[c]	Ce(IV)	0.027	6
$CaMn_3O_6$	Ce(IV)	0.05	7
MnO_2[d]	Ce(IV)	0.09	8
$CaMn_4O_8$	Ce(IV)	0.04	7
MnO_2	Ce(IV)	trace	8
$CaMn_2O_4.4H_2O$	Ce(IV)	0.32	6
$CaMn_2O_4.H_2O$	Ce(IV)	0.54	6
Mn_2O_3[e]	$Ru(bpy)_3^{3+}$	0.22	9
MnO_2 [f]	$Ru(bpy)_3^{3+}$	0.1	9
Mn(III)@Mt[g]	Ce(IV)	0.53	10
$Mn_2O_2(terpy)_2(OH_2)_2$@Mt	Ce(IV)	0.22	10
Co/phosphate/oxide film[h]	Electrochemitry	2.2	11
PSII[i]	Sunlight	25000	12

[a] by suspending the oxidized cubane, $[Mn_4O_4L_6]^+$, into a proton-conducting membrane (Nafion) preadsorbed onto a conducting electrode and electroxidizing the photoreduced butterfly complexes by the application of an external bias [3], [b] dipic = 2,6-pyridinedicarboxylate, [c] surface of compound as 16.6 m^2/g, [d] A soluble form of nano-sized colloidal manganese(IV) oxide, [e,f] Nanostructured manganese oxide clusters supported on mesoporous silica, [g] Mt; K10 montmorillonite,[h] this cobalt compound is added to compare with manganese compounds, [i] based on a rate of 100 O2 per s and PSII in full sunlight and 4 Mn per WOC.

References

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