

Supporting Information

Nano-sized manganese oxide-bovine serum albumin as a promising and biomimetic catalyst for water oxidation

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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-K α radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) was added to 1 mL of concentrated nitric acid and H₂O₂, 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 °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 °C using the method of initial rates from at least 100 s.

Water Oxidation Experiment

Photochemical water oxidation experiments were conducted in a colourless three-neck, round-bottom glass flask (50 ml) containing 40.0 ml of aqueous buffer (acetate and acetic acid, 0.05 M) with pH held at 4.5, 200 mg Na₂S₂O₈, 390 mg Na₂SO₄, and **1** (26.0 mg). One neck of the flask was closed by a septum (rubber stopper) after deaeration with argon whilst the sensor of the oxygen meter (HQ40d) was introduced into the solution through the other neck of the flask, to measure the amount of oxygen evolved during the irradiation. The third neck was used to introduce an aqueous suspension containing several particles of **1** into the reaction flask. To show that no oxygen entered the reaction flask due to an air leak, the reactor was maintained in the dark for 10 min prior to irradiation while oxygen levels in the flask were

monitored. The irradiation of the aqueous reaction mixtures containing **1** was carried out while the reaction flask (reactor) was maintained in a methacrylate thermostatted water bath at 25.0 °C. The irradiation was with visible light ($\lambda > 400$ nm) from a 250W tungsten lamp. The illumination intensity was ~5,000 lux as determined with a MS-1300A luxmeter. A cut-off light filter (was placed between the light source and the sample in the reactor to ensure that only visible light ($\lambda > 400$ nm) reached the samples.

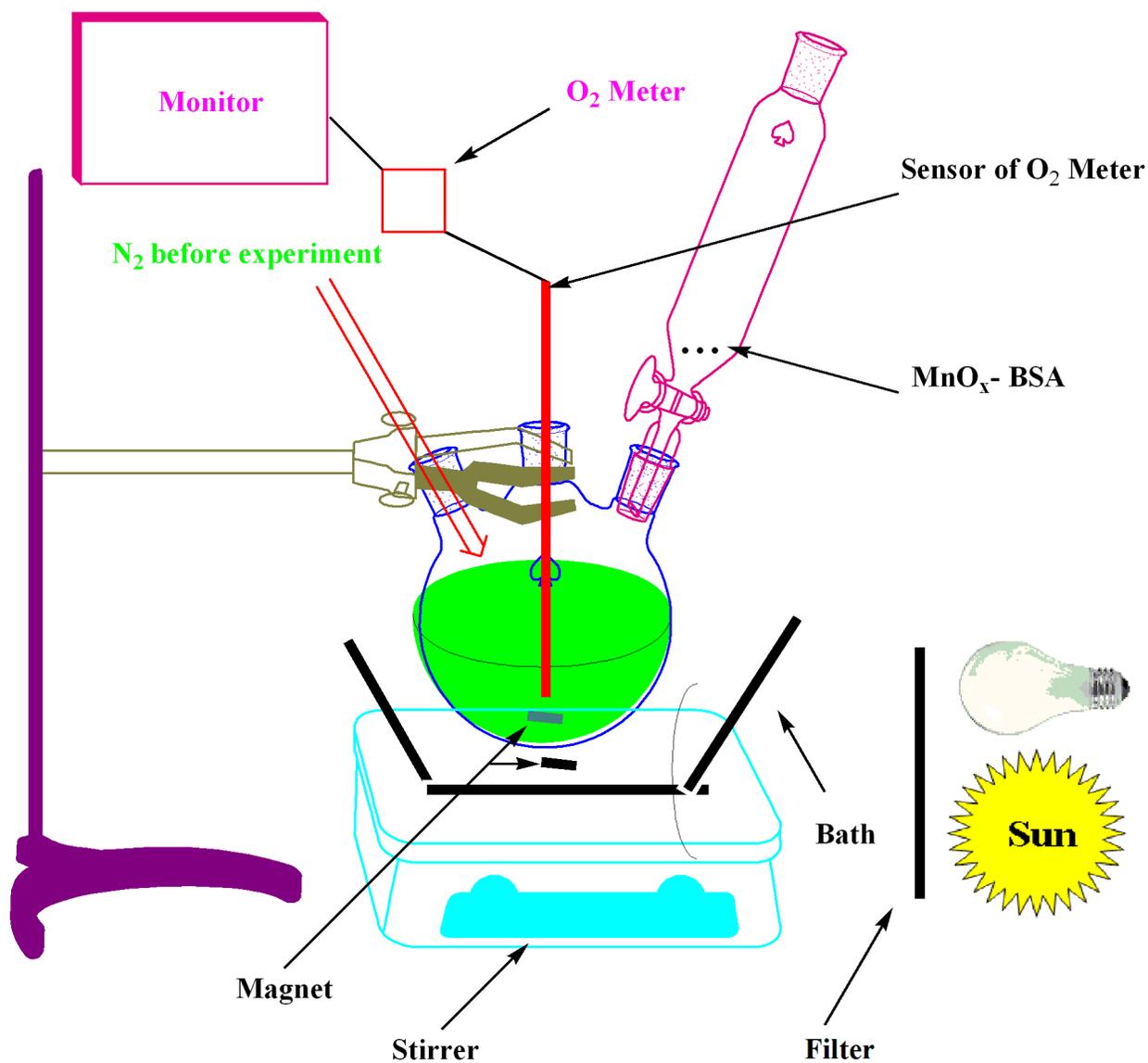


Fig. S1. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence of tris(2,2'-bipyridyl)ruthenium(II) chloride, chloro pentaammine cobalt(III) chloride, in acetate buffer in the presence of light (from a bulb) ($\lambda > 400$ nm).

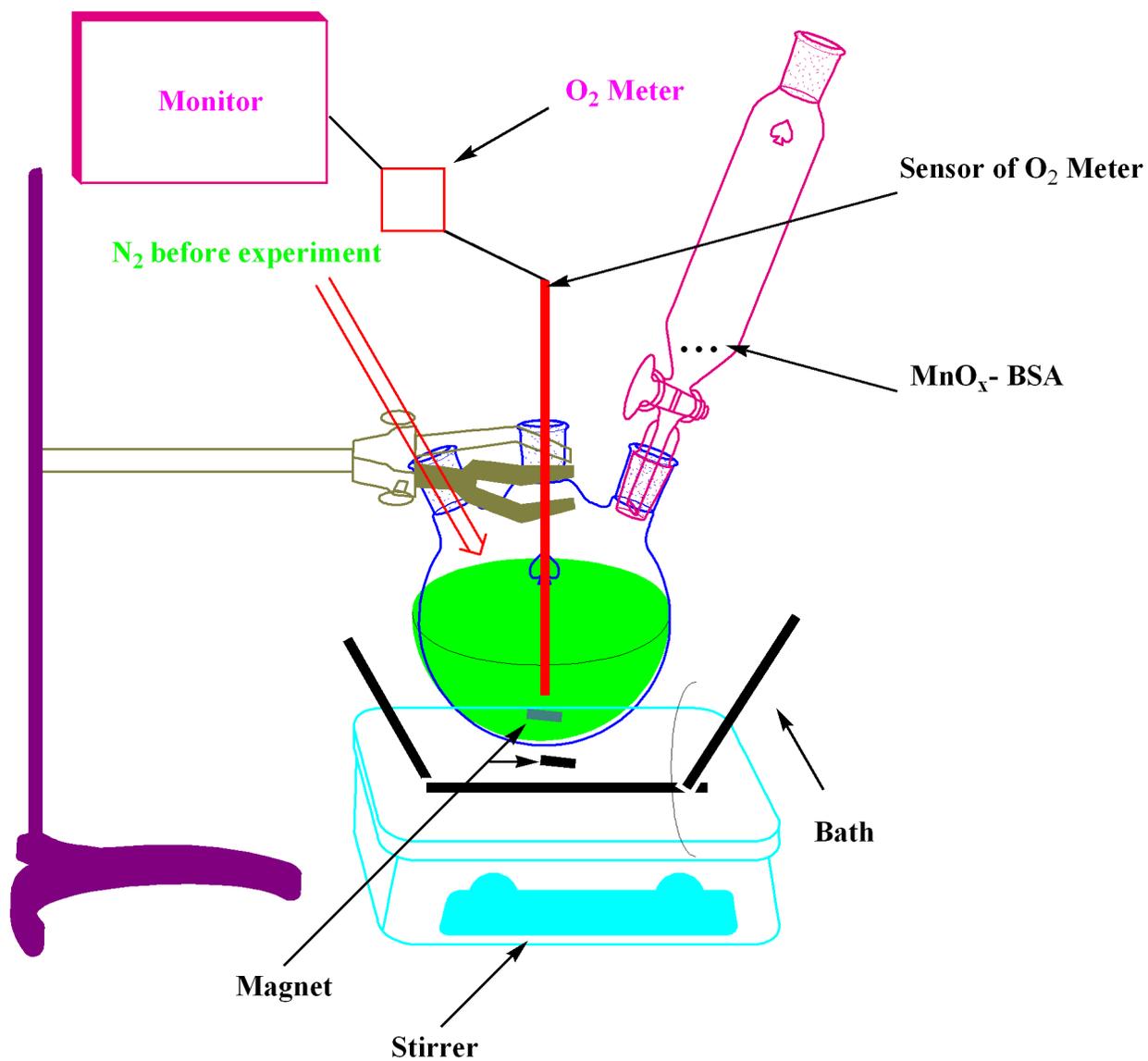


Fig. S2. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence of $(NH_4)_2Ce(NO_3)_6$.

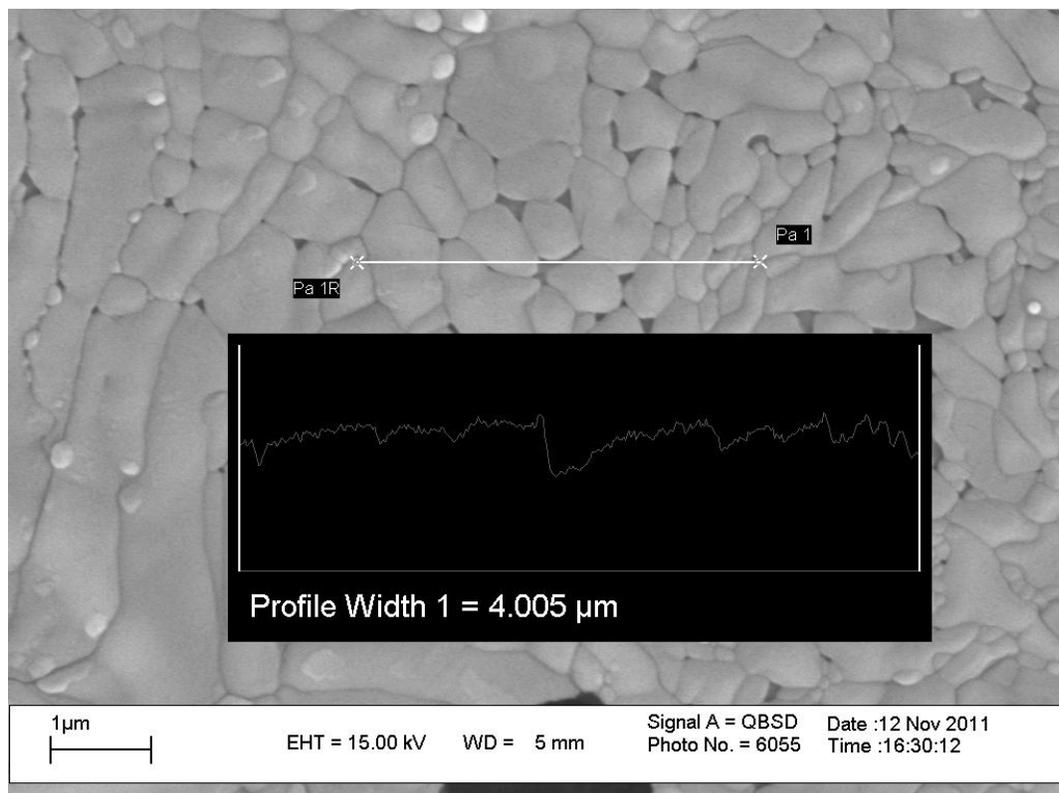
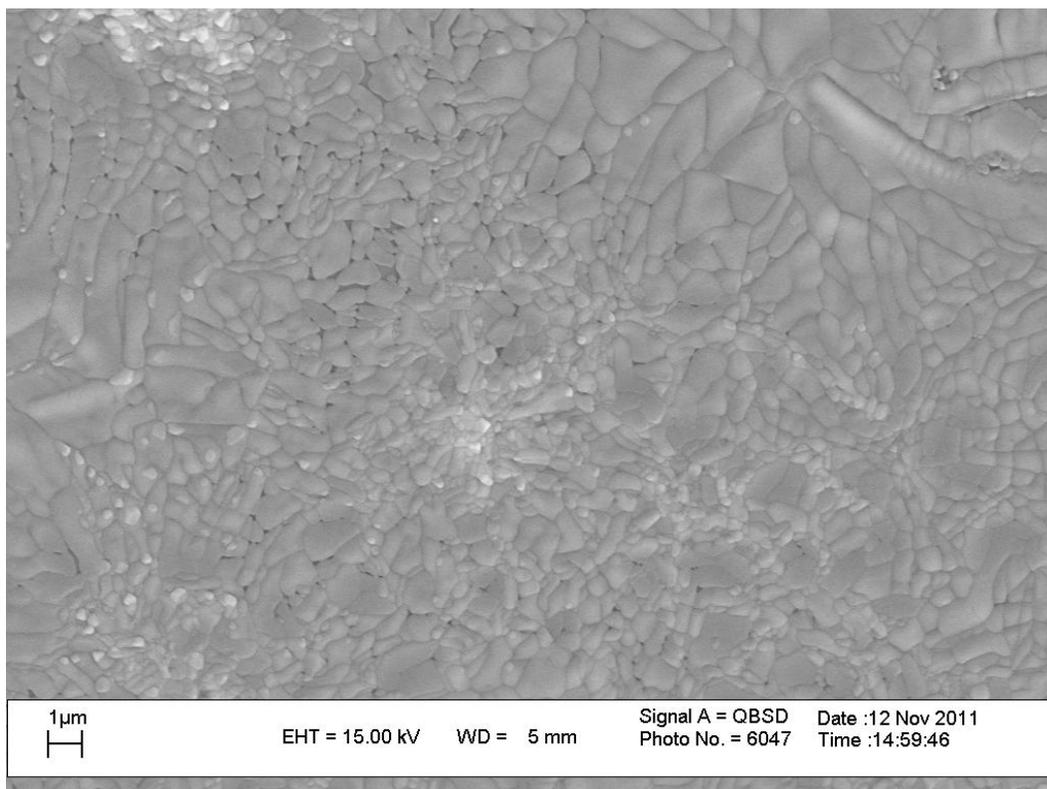


Fig. S3. The SEM images from nano manganese oxide - Bovine Serum Albumin film.



Fig. S4. Drying the solution contains nano manganese oxide - Bovine Serum in air and at room temperature produced a film.

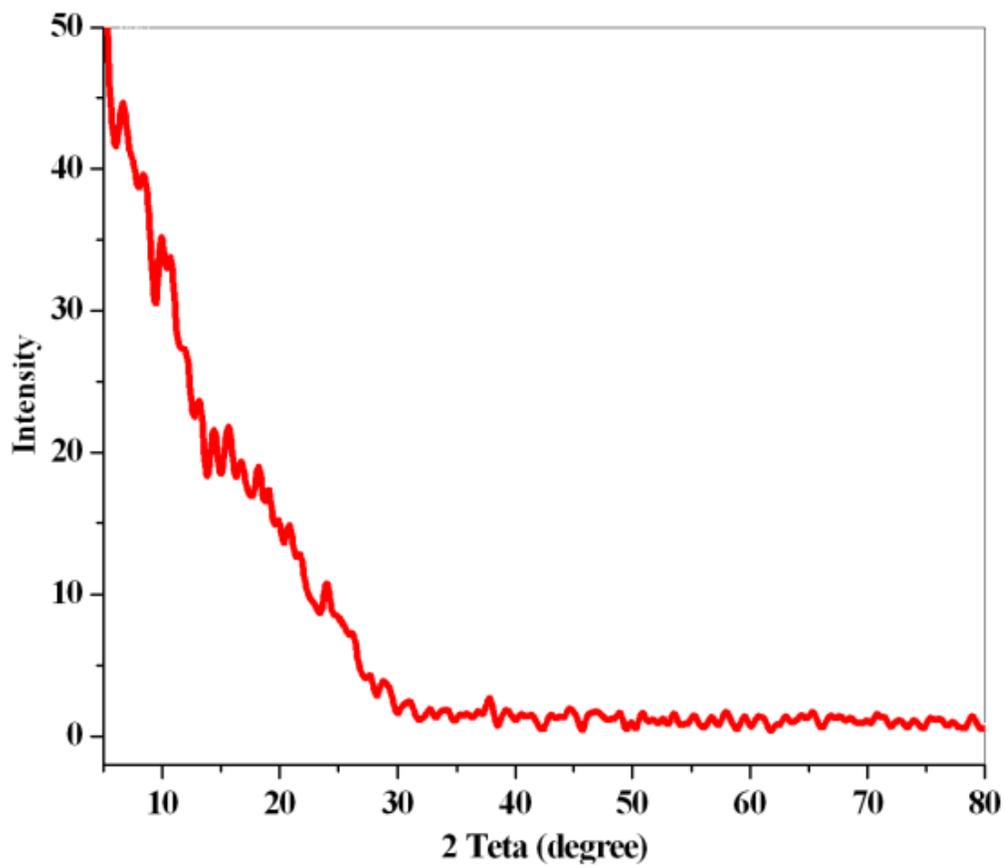
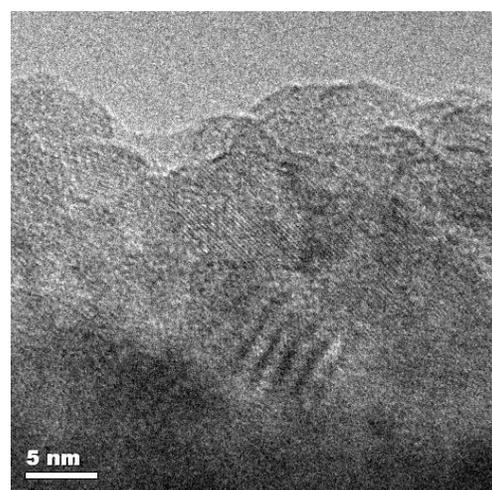
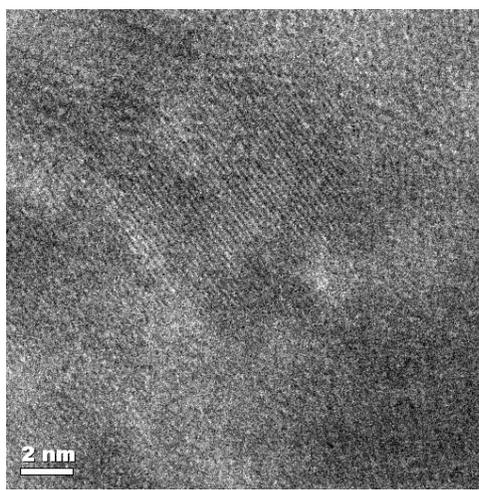
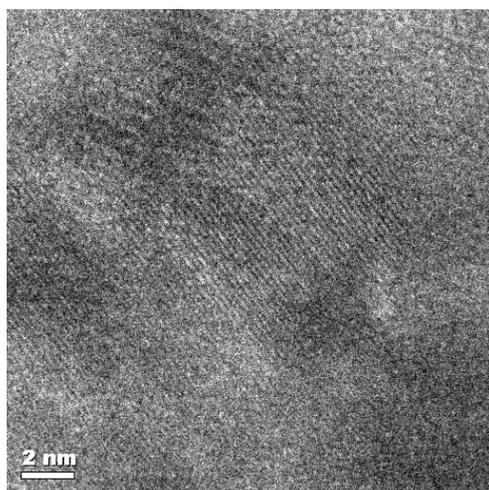
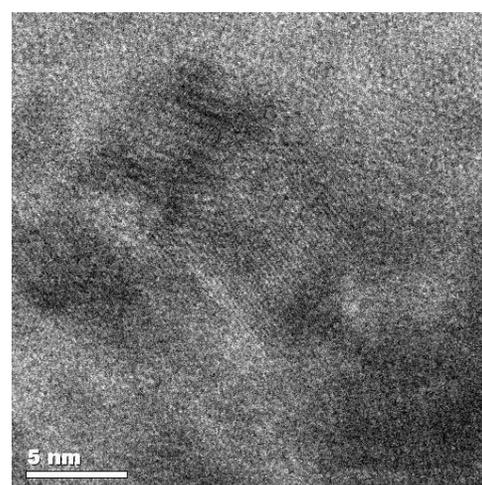
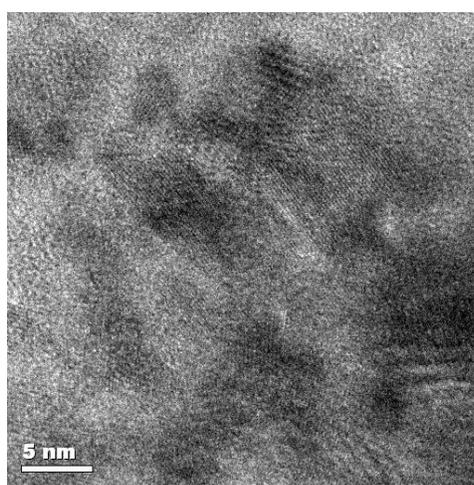
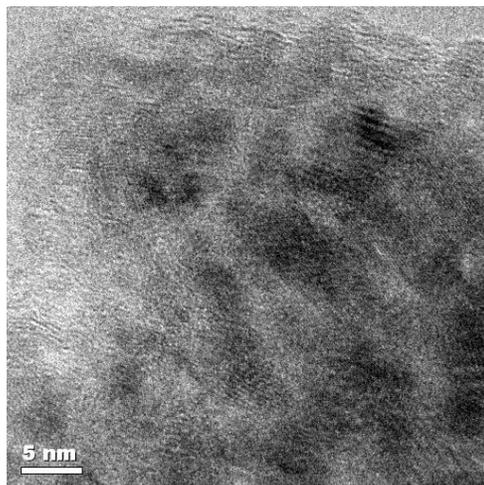
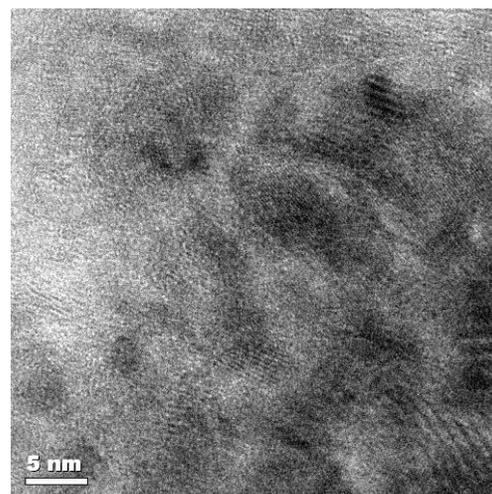
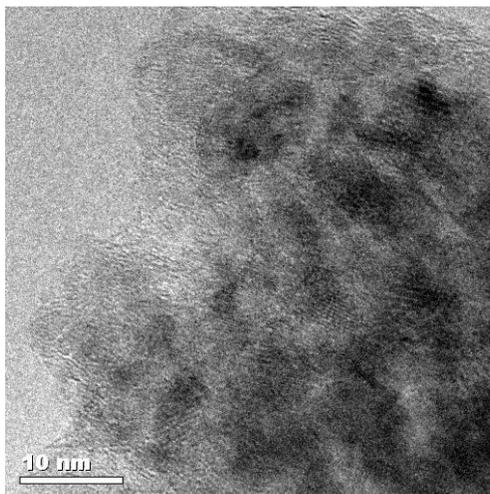
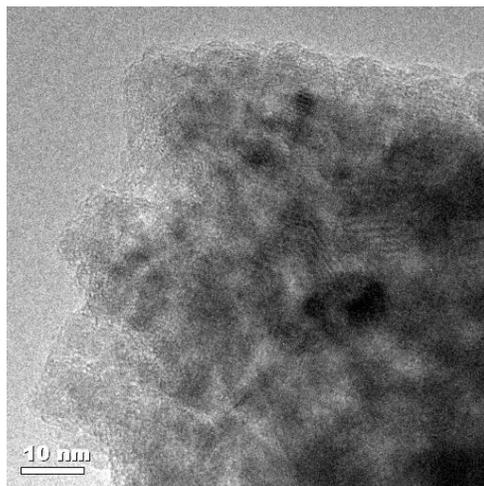


Fig. S5. Powder X-ray diffraction patterns of a solution of nano manganese oxide - Bovine Serum.



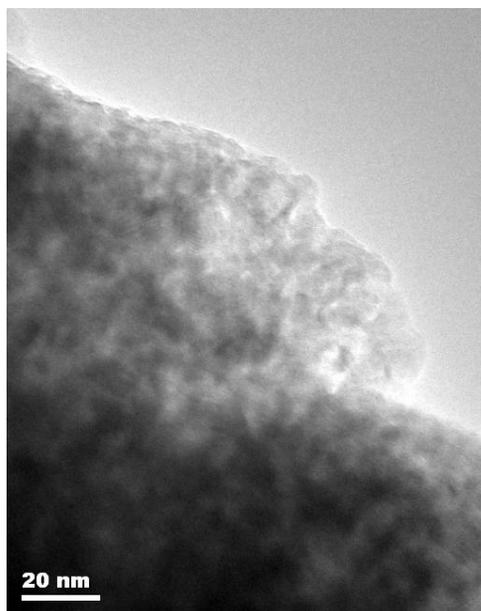
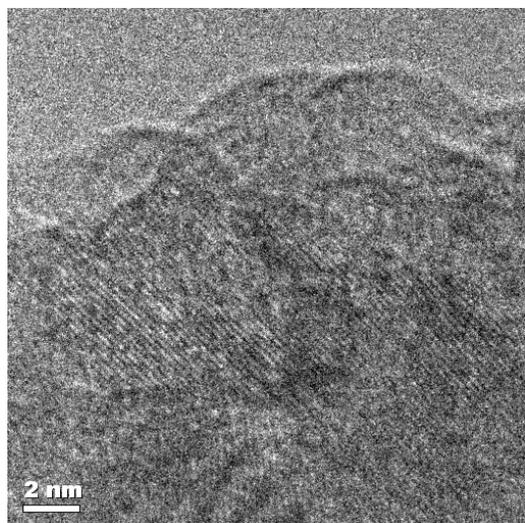
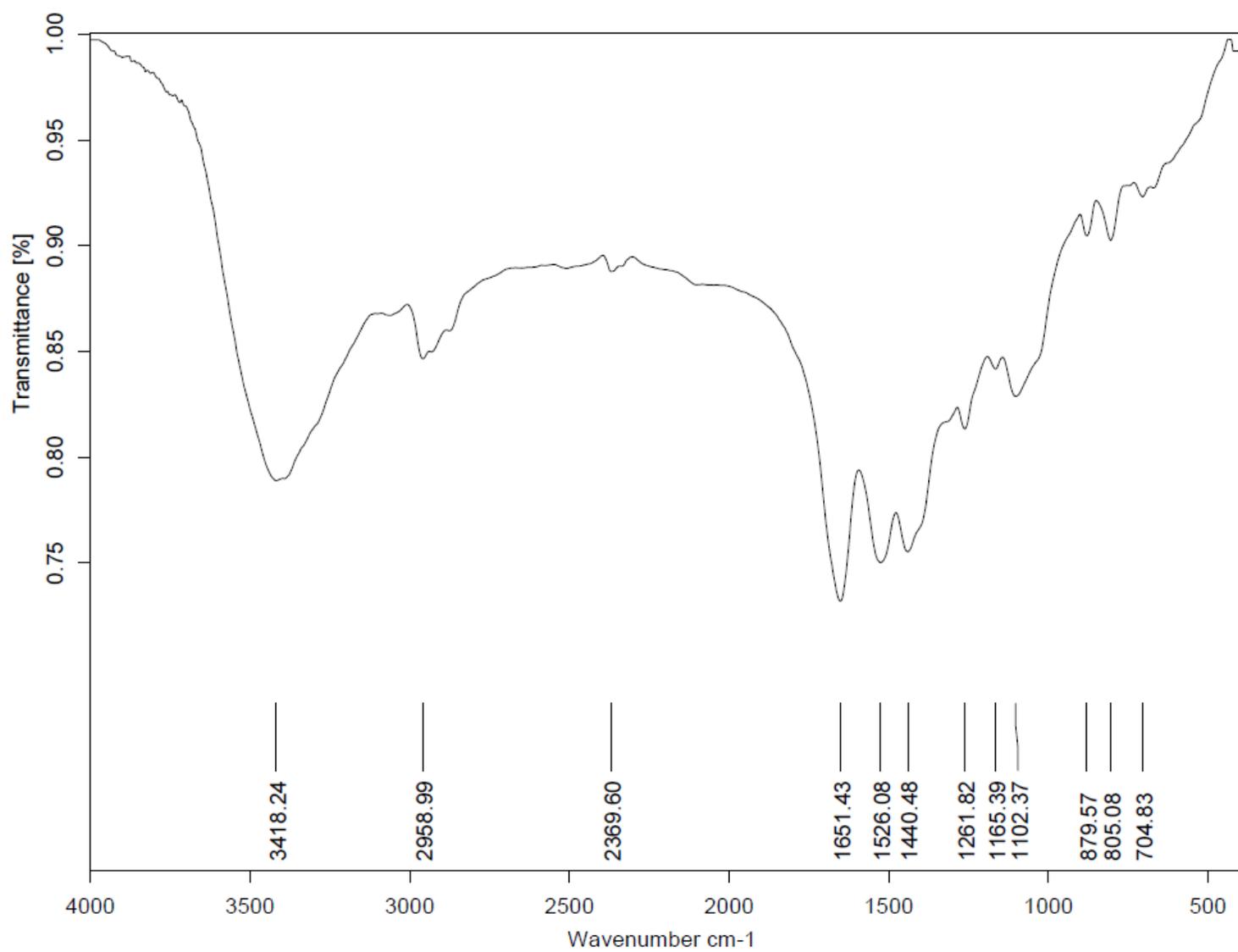
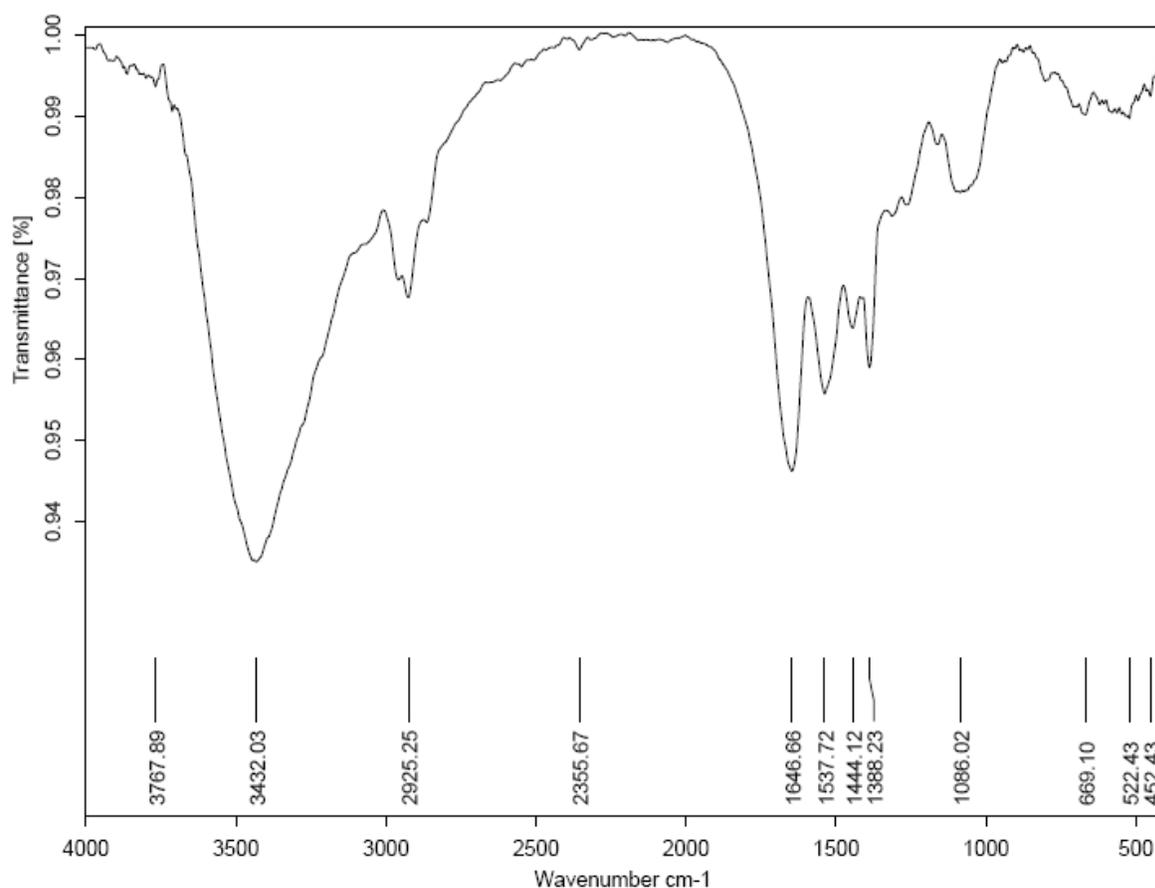


Fig. S6 HRTEM images of manganese oxide – BSA film.



(a)



(b)

Fig. S7 IR spectrum of BSA (a) and Nano manganese oxide - Bovine Serum Albumin film (b). The intensities of these peaks reduced in higher temperature. The absorption bands characteristic for a MnO_6 core in the region $400 - 500 \text{ cm}^{-1}$ assigned to stretching vibrations of Mn-O bonds in manganese oxide was also observed in the FTIR spectra of these compounds.²

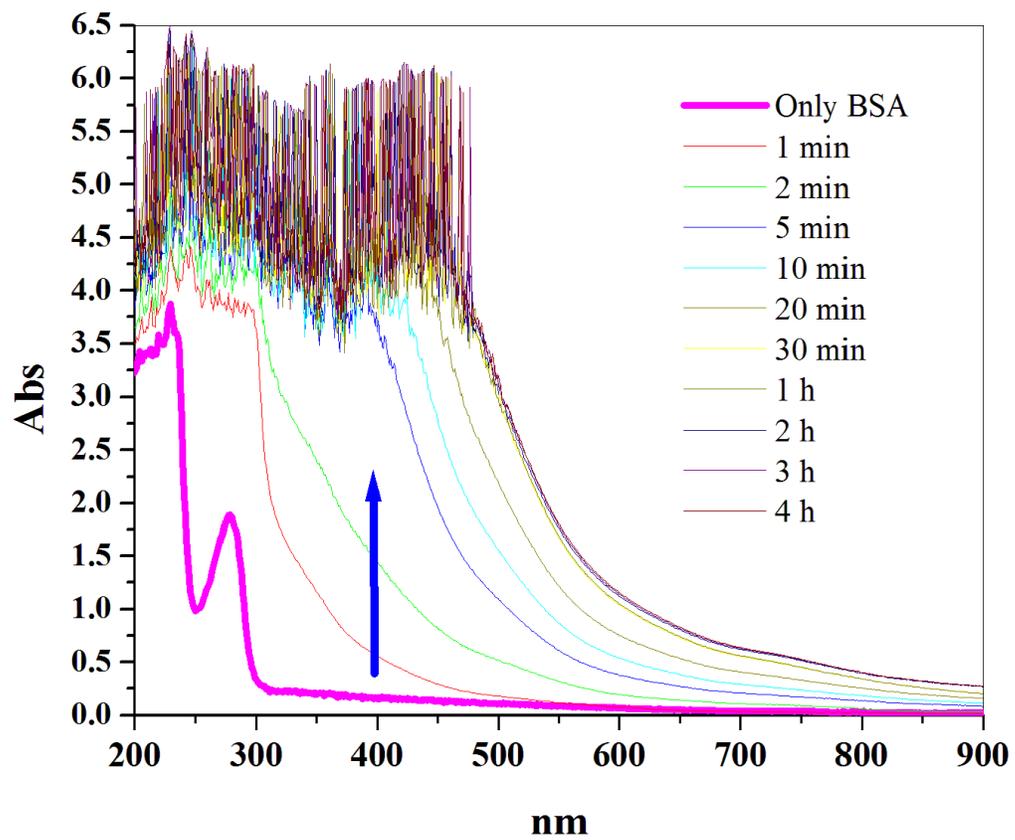


Fig. S8 UV-Vis spectra of BSA and BSA-MnCl₂ + KMnO₄. Arrow show a peak at ~ 400 nm related to Mn oxides.⁸

Table S1 The rate of water oxidation by the various manganese oxides as catalysts for water oxidation.

Compound	Oxidant	TOF ^a	References
Nano manganese oxide - Bovine Serum Albumin	Ru(bpy) ₃ ³⁺	0.14	This work
	Ce(IV)	0.27	
Octahedral Molecular Sieves	Ru(bpy) ₃ ³⁺	0.11	1
	Ce(IV)	0.05	
Octahedral Layered	Ru(bpy) ₃ ³⁺	0.028	1
	Ce(IV)	0.0047	
Amorphous Manganese Oxides	Ru(bpy) ₃ ³⁺	0.06	1
	Ce(IV)	0.52	
CaMnO ₃	Ce(IV)	0.012	2
Ca ₂ Mn ₃ O ₈	Ce(IV)	0.016	2
CaMn ₂ O ₄ .H ₂ O (Nano particles)	Ce(IV)	2.2	3
CaMn ₃ O ₆	Ce(IV)	0.046	4
CaMn ₄ O ₈	Ce(IV)	0.035	4
CaMn ₂ O ₄ .4H ₂ O	Ce(IV)	0.32	5
CaMn ₂ O ₄ .H ₂ O	Ce(IV)	0.54	5
Mn ₂ O ₃	Ce(IV)	0.027	5
α-MnO ₂ nanotubes	Ru(bpy) ₃ ³⁺	0.035	6
α-MnO ₂ nanowires	Ru(bpy) ₃ ³⁺	0.059	6
β-MnO ₂ nanowires	Ru(bpy) ₃ ³⁺	0.02	6
Bulk α-MnO ₂	Ru(bpy) ₃ ³⁺	0.01	6
Mn oxide nanoclusters	Ru(bpy) ₃ ³⁺	0.28	7
MnO ₂ (colloid)	Ce(IV)	0.09	8
PSII	Sunlight	25000	9

^a mmol O₂/mol Mn per second. In these calculations, it is assumed that all deposited metal centers are involved in the catalysis, so lower TOF limits are calculated.

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