

Supporting Information

Experimental

Material

All chemicals used in the syntheses were purchased from Merck or Aldrich and were used without further purification. All solutions were prepared using doubly deionized water.

Water oxidation

Photochemical water oxidation experiments were conducted in a colourless three-neck, round-bottom glass flask (50 ml) containing 40 ml of aqueous buffer (acetate and acetic acid, 0.5 M) with pH held at 4.0, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (10.0 mM), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mM), and manganese oxide (0.37 mM). One neck of the flask was closed by a septum (rubber stopper) after deaeration with nitrogen whilst the sensor of the oxygen meter 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 manganese oxides 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 manganese oxides was carried out while the reaction flask (reactor) was maintained in a thermostatted water bath at 25.0 °C. The irradiation was with visible light ($\lambda > 400$ nm) from a 500W tungsten lamp. The illumination intensity was ~10,000 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).

Oxygen evolution from aqueous solutions in the presence of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (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 °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 a solution of manganese oxide (40 ml, 0.57 mM). Then Ce(IV) (10 ml, 0.5M) solution - after deaeration of Ce(IV) with nitrogen – add to the solution of manganese oxide and oxygen evolution were recorded with the oxygen meter under stirring (Fig. S1). Oxone was standardized by iodometric titration and found to contain 0.21 mmol KHSO_5 per 100 mg. The acetate buffer was prepared by adjusting the pH of a 0.1 M KOAc solution to 4.5 with concentrated H_2SO_4 . In a typical experiment, after the deaeration with nitrogen, manganese oxide (20 ml, 0.46 mM) was added to a buffered solution of oxone solution (20 ml, 0.015 M in 0.01 M acetate buffer, pH 4.5).

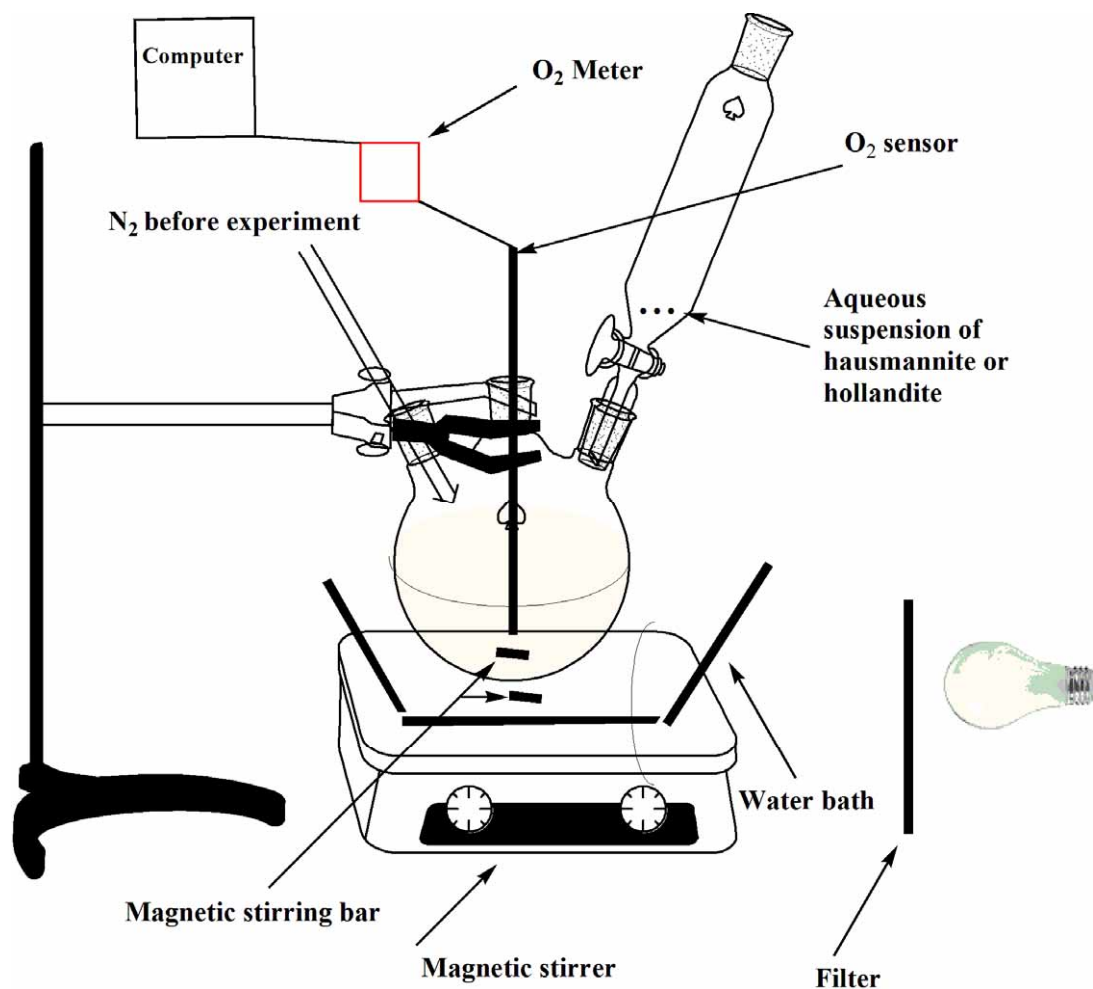


Fig. S1. The reactor set-up for oxygen evolution experiment. In the case of oxygen evolution experiment with Ce(IV), oxone or H₂O₂ as an oxidant there are no need to filter and bulb in this set-up.

Synthesis of compound

The colloidal manganese oxide was synthesised by a similar method to the one described by Perez-Benito et al. [1]. Water-soluble colloidal manganese dioxide was prepared by reducing potassium permanganate with sodium thiosulfate in neutral aqueous solution and a stoichiometric ratio 8:3 [1].

References

- [1] J.F. Perez-Benito, E. Brillas, R. Pouplana, *Inorg. Chem.*, 1989, 28, 390.