

Electronic Supplementary Information.

Photodamage of the manganese-calcium oxide: A model for UV-induced photodamage of the water oxidizing complex in photosystem II

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Experimental

Materials

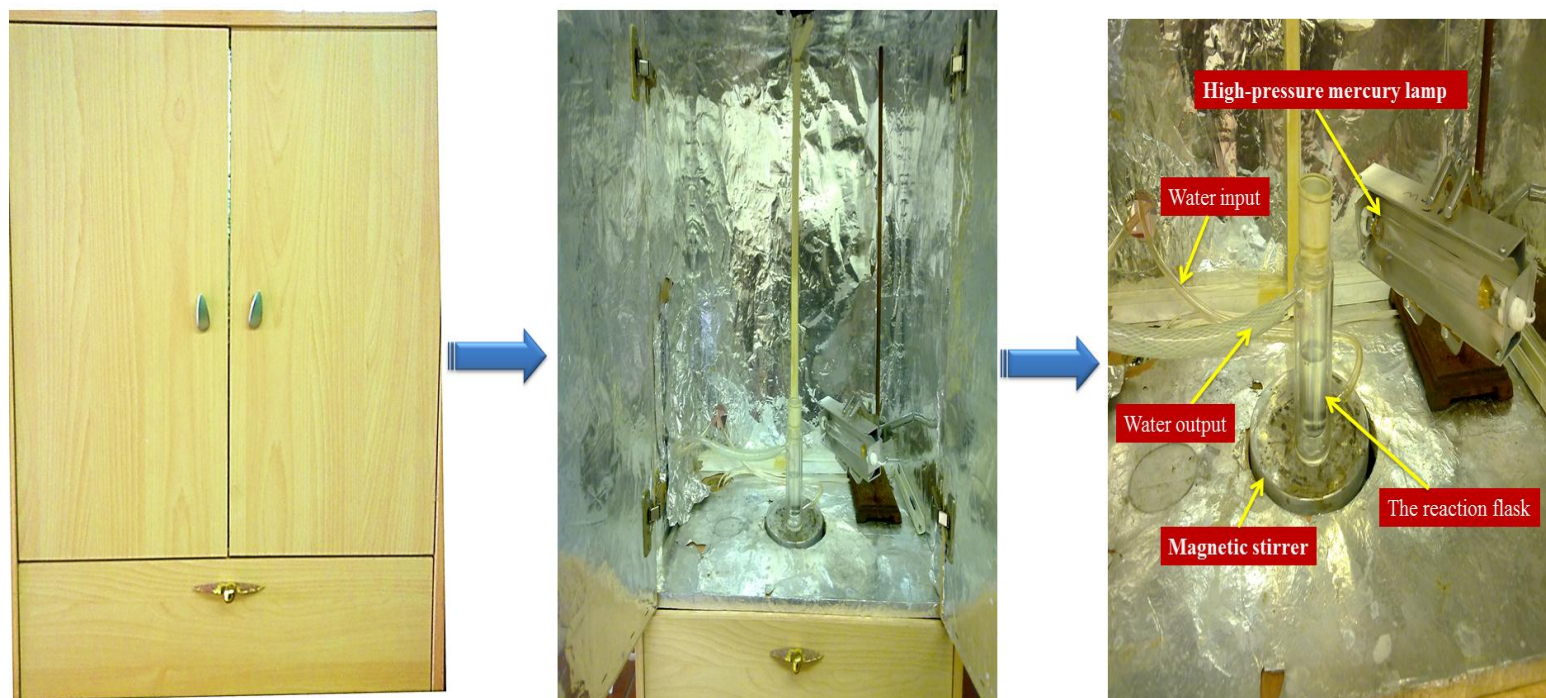
All reagents were purchased from commercial sources and were used without further purification.

Characterization

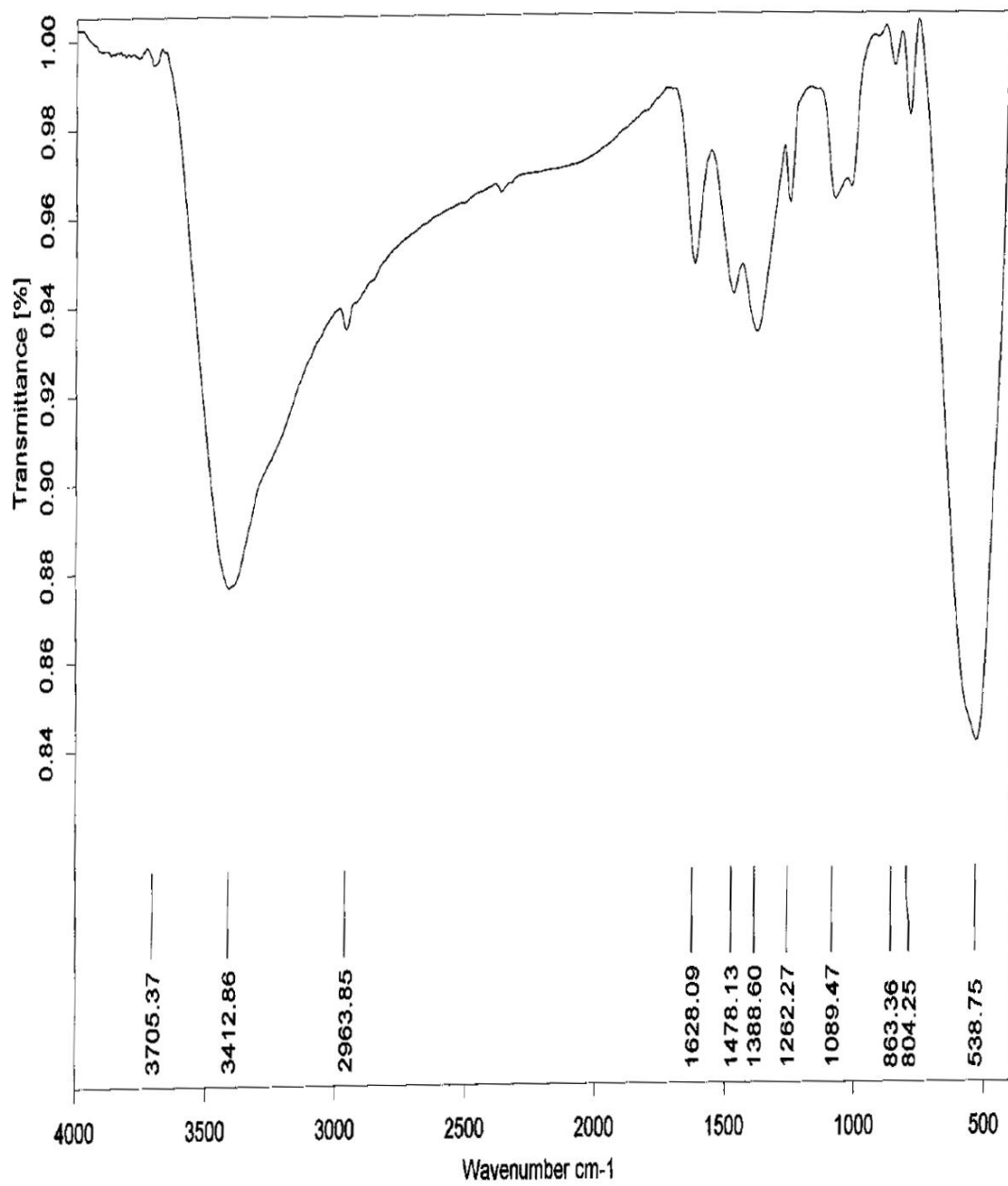
MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400-4000 cm^{-1} . TEM and SEM images were obtained with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-K α radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (2.0 mg) were added to concentrated nitric acid and H₂O₂, left at room temperature to ensure that the oxides were completely dissolved. The solutions were then diluted to 50.0 or 100.0 mL and analysed by AAS.

Photochemical experiments

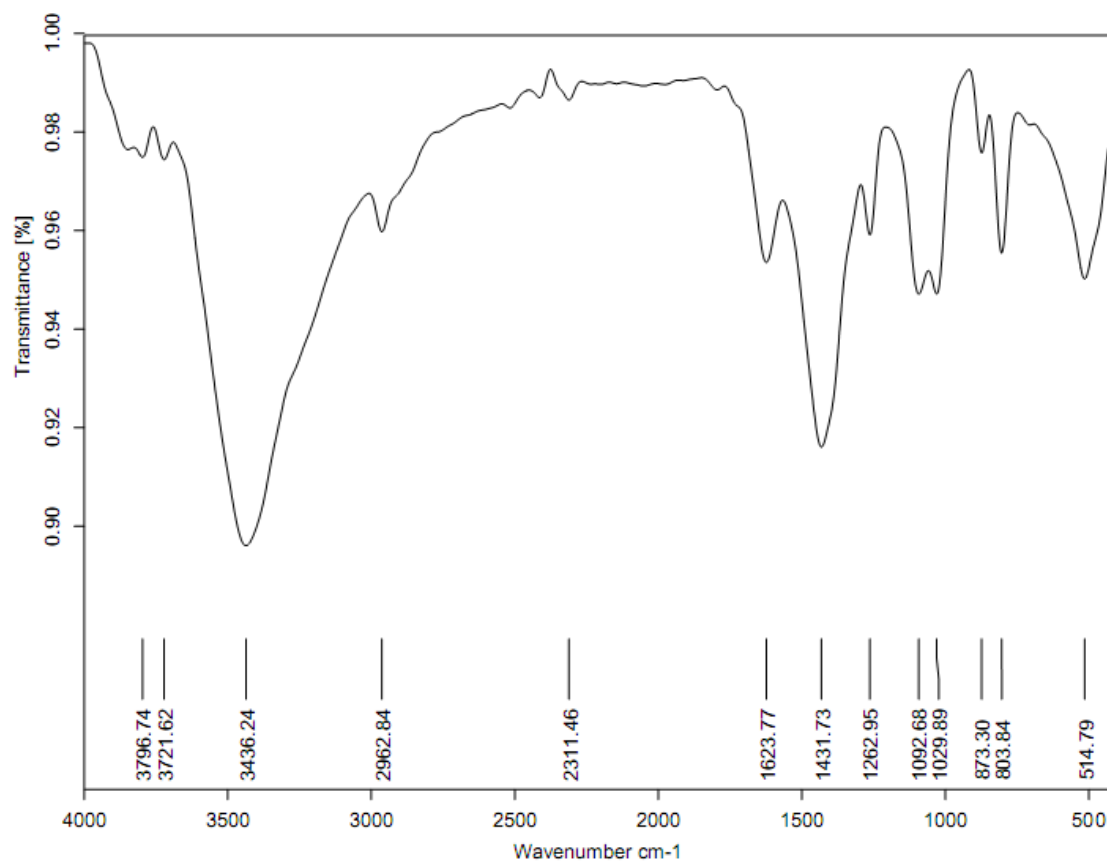
Photocatalytic reactions were carried out in a cylindrical round bottomed quartz photo-reactor and irradiated using 300 W high pressure mercury lamp under magnetic stirring at room temperature (Scheme S1).



Scheme S1 The set up for photochemical experiments.



a



b

Fig. S2 IR spectra for Mn-Ca oxide (a) and Mn-Ca oxide after treatment with aspartic acid. The bands in 1431-1500 cm^{-1} could show that carboxylate groups coordinate to Mn-Ca ions of Mn-Ca oxide in a bridging mode (b).¹

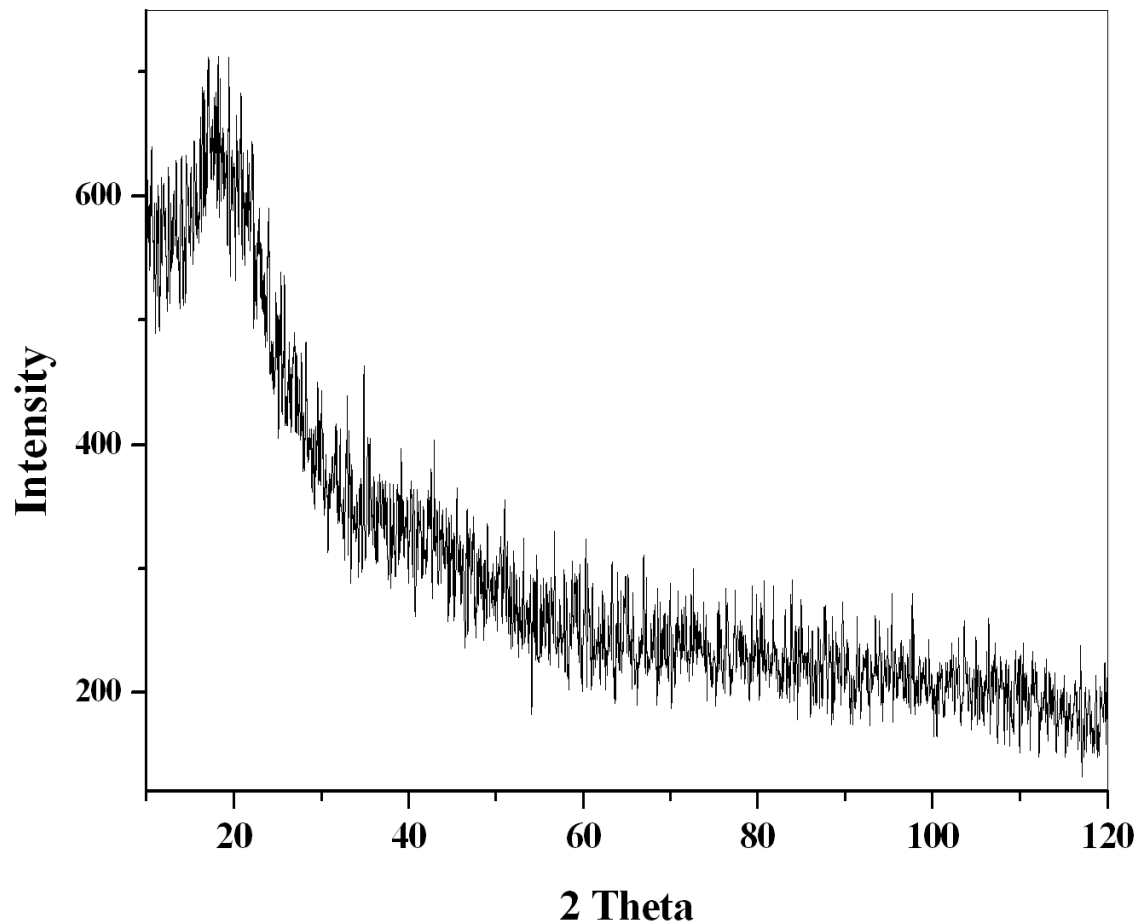


Fig. S3 XRD patterns of the nano-sized manganese-calcium oxide after heating at 500 °C for 10 h.

Reference:

1.K. Nakamoto in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, sixth edition, A Wiley-Interscience Publication, 2009, 64-65.