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# Electronic Supporting Information

## Exploring effects of intermittent light upon visible light promoted water oxidations

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## Powder X-ray analysis of metal oxide catalysts

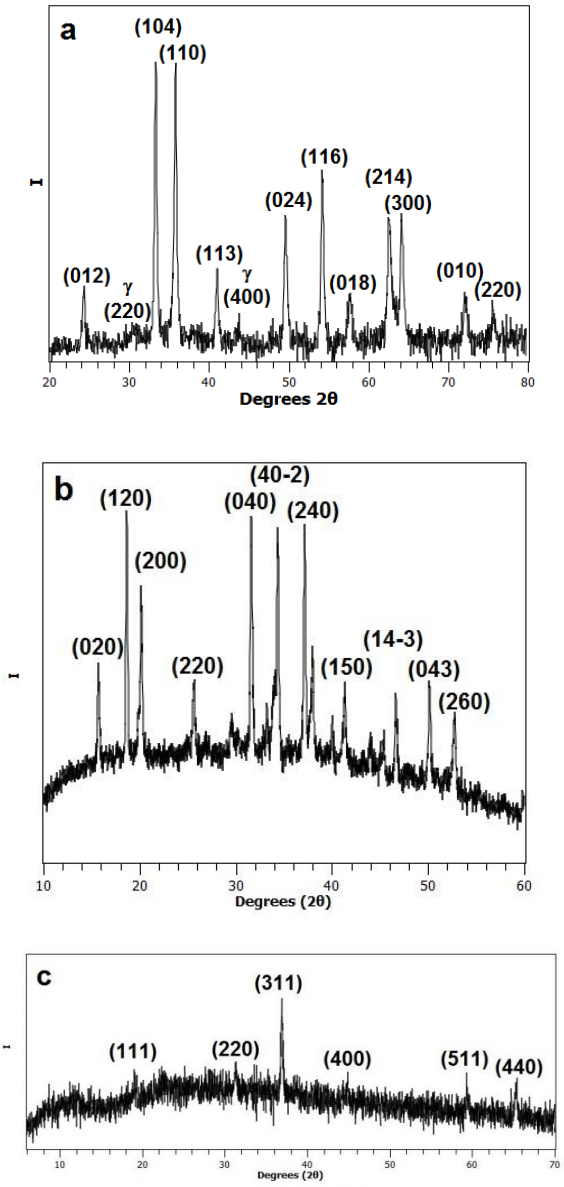



Fig. S1. Powder X-ray analysis of prepared samples of (a) α/γ $Fe_2O_3$ ( hematite JCPDS 013-0534/ trace level of maghemite, JCPDS 024-081); [1] (b) $CaMn_3O_6$ – structure was consistent to the known crystal structure [2] and Miller indices determined with Mercury 3.9 CCDC crystallographic software; (c) commercial laser ablated $Co_3O_4$ sample (JCPDS 00-042-1467).

## Preparation of metal oxides

### Preparation of $Fe_2O_3$

The preparation of the mixed phase α/γ-$Fe_2O_3$ has been described in detail previously.[1] Briefly iron nitrate (8g) was dissolved in 75ml of DI water, 3g of xyloglucan was then slowly added and dissolved to give a viscous mixture. The dried mixture was heated (at 20ºC/ min) to 500ºC and then held at this temperature for 10 min. A red/ orange powder was obtained, this was lightly hand ground in an agate pestle and mortar before use as a catalyst on the photocatalyzed water oxidations. indicated by powder XRD analysis that the hematite (110) reflection was moderately enhanced by use of the templating synthesis as peak intensity was equivalent to the (104) plane. An enhanced (110) plane is associated with improved water splitting efficiency.[3]

### Preparation of $CaMn_3O_6$

8 g of dextran (MW70k) was dissolved in 70 ml of DI $H_2O$, 4.00 g of $Mn(NO_3)_2.4H_2O$ and 1.25 g of $Ca(NO_3)_2.4H_2O$ were then dissolved in the mixture to give a molar ratio of Ca:Mn of 1:3. [4] The mixture was air dried then heated in a furnace to 800ºC at 10ºC $min^{-1}$. The black coloured powder was lightly ground in an agate mortar before use.

### Cobalt oxide

A commercial laser ablated $Co_3O_4$ (Sigma-Aldrich 637025, measured $S_{BET}$ = 35.8$m^2$ $g^{-1}$) was also used for comparison in photocatalytic water oxidations, the black powder was lightly ground in an agate mortar before use.

## Photocatalytic water oxidations

Nitrogen degassed DI water was used to prepare an acetate buffer of pH 5.2 (50mM sodium acetate adjusted with acetic acid). A custom made three arm 50ml glass flask was taken and 125 mg of $[Co(NH_3)_5Cl]Cl_2$ electron acceptor and 45mg $[Ru(bipy)_3]Cl_2.6H_2O$ (99.95%) sensitizer added together with 20ml of buffer. The reaction flask was covered with foil to shield from light and stirred for 5 minutes to allow the electron acceptor to fully dissolve. 10mg of the metal oxide catalyst suspended in a further 15ml of the degassed buffer was then added. The light shielded reaction flask was then left stirring for 20 minutes for the system to equilibrate. The light shield covering was then removed and the stirred flask illuminated by a 3W blue light LED ($\lambda_{max}$ 448nm) held at a specific distance from the edge of the reaction flask to give a generated measured output of 5mW$cm^{-2}$ (Solartech Inc. Solar Meter 9.4), at the reaction flask (with measured LED light exposed surface area of 31.5$cm^2$).

This light source was connected to a DC-DC step down power supply connected to an input of 12V DC and output set at constant 3.37 V. This in turn was attached to a programmable FRM01 timer module connected to the LED light that allowed programmable timing of light on : off intervals accurate to ±0.005s.

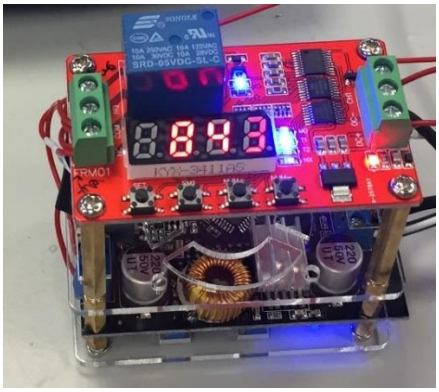


Image of DC-DC step down constant power supply linked to timer module to supply constant voltage and accurate on:off light timing to LED light source

Gaseous $O_2$ release was monitored using a Pyroscience Firesting O2 fibre optic $O_2$ sensor with an OXYROB10 oxygen probe together with a TDIP temperature sensor to give automatic compensation for minor fluctuations in reaction flask temperature (<±0.5°C for 60 min reaction). $O_2$ readings at 10s intervals were recorded to minimize possible photobleaching effects on the $O_2$ sensor. These probes were fitted into the flask aperture and reactions in air were conducted in the flask ($O_2$ level was zeroed after equilibration).

$O_2$ production after light on was monitored for 60 minutes. Micromoles of $O_2$ gas released into the known headspace volume was calculated from measured $O_2$ ppm increase. The reaction mixture pH was also simultaneously monitored using a Eutech Cyberscan pH450 with USB output to PC. Samples runs were conducted in triplicate with representative $O_2$ and proton release profiles shown.

Maximum theoretical yield of $O_2$ based on electron acceptor concentration = (125mg/250.4)/ 4 mol = 124.8μmol $O_2$.

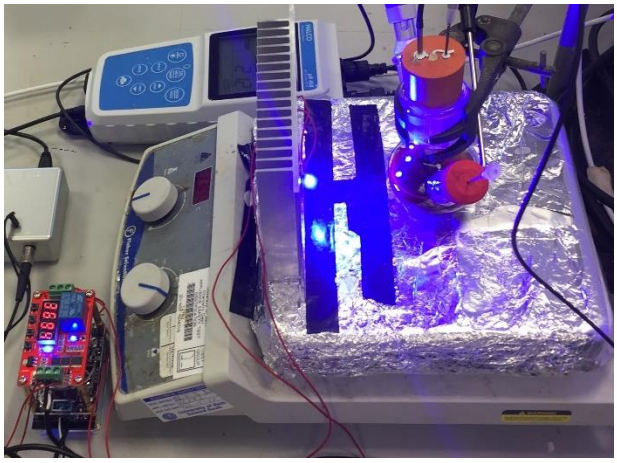


Image of photocatalytic reaction set-up with flask containing pH probe in stirred reaction mixture and $O_2$ and linked temperature compensation sensor probes located in headspace. These are linked to the Firesting O2 sensor unit and then onto a PC for in-situ real-time measurements. The LED is linked to a DC supply and timer module. The reaction flask and LED mounted on a heat sink are held at fixed

positions to ensure consistent measurements. A solar meter was use measure light was at 5mWcm$^{-2}$ at the position of flask outer surface facing the LED light source.

During a photocatalyzed water oxidation the $[Co(NH_3)_5Cl]Cl_2$ electron acceptor decomposes with release of ammonia and $Co(OH)_2$.[5]

$$[\boldsymbol{Co}(\boldsymbol{NH_3})_5\boldsymbol{Cl}]^{2+} + [\boldsymbol{Ru}(\boldsymbol{bpy})_3]^{2+*} \rightarrow [\boldsymbol{Ru}(\boldsymbol{bpy})_3]^{3+} + \boldsymbol{Co}^{2+} + \boldsymbol{5NH_3} + \boldsymbol{Cl}^{-}$$

Control experiments in absence of light sensitizer, catalyst and light were conducted, oxygen production was not detectable in the absence of light or light sensitizer. In absence of catalyst a very low level of $O_2$ was detected after a prolonged lag phase due some self-decomposition of the ruthenium dye sensitizer and its conversion into a weakly active catalyst.

**Collection of samples for mass spectrometry analysis**

For MS analysis of reaction mixtures 1ml of the stirred reaction mixture following 60 min photocatalysis was filtered through a 0.22μM syringe filter. 0.1ml of this was added to 1ml HPLC grade methanol. In each case a further dilution 1:1000 in HPLC grade methanol was used for mass spectrometry (MS) analysis. For MS of deposits formed of the flask lateral surface, in each case the reaction mixture and a further 20ml of DI rinsing water were decanted. The deposit which remained adhered to the flask was then collected by careful collection into 5ml of HPLC grade methanol. This was then filtered through 0.22μM syringe filter. In each case a further 1:500 dilution of the filtered solution with HPLC grade methanol was used for MS analysis. The $[Co(NH_3)_5Cl]Cl_2$ reagent is essentially insoluble in methanol hence collected MS spectra are generated by $[Ru(bpy)_3]^{2+}$ and its decomposition products (together with any additional methanol soluble breakdown products derived from the pentamine complex).

**Effect of acidic conditions on $CaMn_3O_6$ catalyst**

To determine the effect of mild acid conditions on the composition of the $CaMn_3O_6$ catalyst, a 10mg sample was taken and suspended in 35ml of stirred acetate buffer of pH 5.5 for 10 min. EDX analysis was then conducted of the untreated catalyst in comparison to the mild acid treated sample. Samples were prepared as powder samples on carbon tape mounted on aluminium stubs was conducted on a Jeol 6480 LV SEM operating at 20eV. Quantitative analysis of Ca, Mn and O was conducted using Oxford Instruments INCA software, the EDX was calibrated with copper and iron samples prior to analysis. Analysis in triplicate (each of four iterations) of representative areas was conducted for each sample. Representative EDX spectra shown in Fig. S2a,b and a table of measured weight and atomic % shown in Table S1.

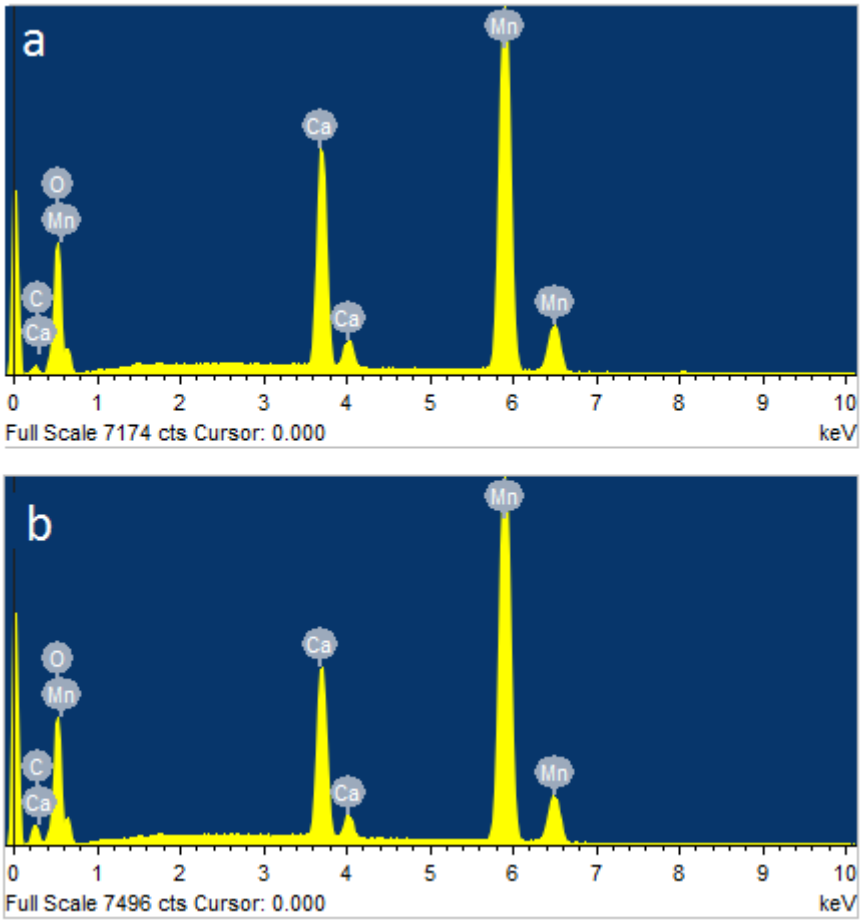
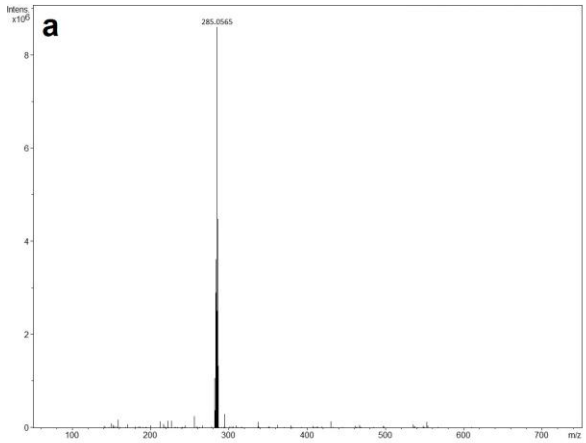


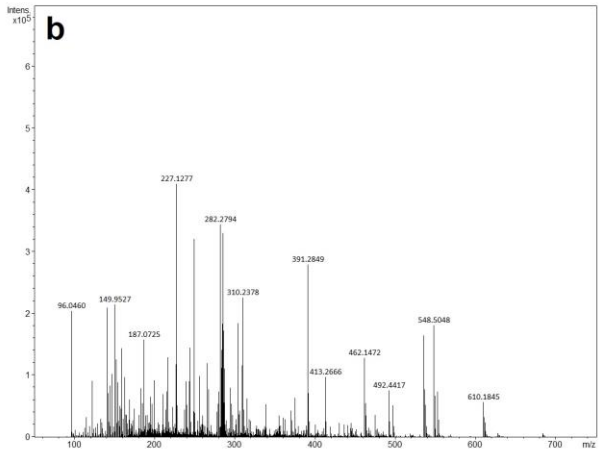

Fig. S2. Images of representative EDX spectra of the $CaMn_3O_6$ catalyst used in photocatalytic water oxidations showing; (a) Untreated $CaMn_3O_6$; (b) $CaMn_3O_6$ after stirring in acetate buffer of pH 5.5 for 10 min.

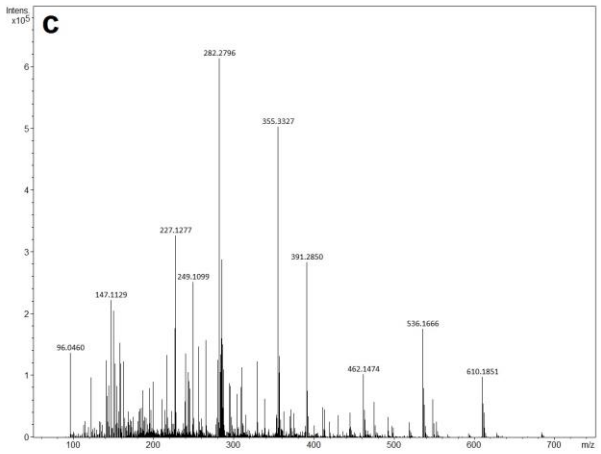
| Untreated $CaMn_3O_6$ catalyst sample | | | |
|---|---|---|---|
| **Weight %** | | **Atomic %** | |
| **Ca** | **Mn** | **Ca** | **Mn** |
| **14.38** | **60.19** | **11.61** | **35.45** |
| **13.92** | **62.58** | **11.24** | **36.85** |
| **14.04** | **57.09** | **10.76** | **31.92** |
| **14.11** | **59.95** | **11.20** | **34.74** |
| | | **Mn:Ca of 3.10:1** | |
| **Weak acid treated $CaMn_3O_6$ catalyst sample** | | | |
| **Weight %** | | **Atomic %** | |
| **Ca** | **Mn** | **Ca** | **Mn** |
| **11.52** | **60.77** | **8.85** | **34.04** |
| **10.74** | **57.38** | **7.71** | **38.54** |
| **12.07** | **63.91** | **9.97** | **34.21** |
| **11.44** | **60.68** | **8.84** | **34.21** |
| | | **Mn:Ca of 3.87:1** | |

Table. S1. Table of repeat measurements of weight and atomic % calcium and manganese by quantitative EDX analysis showing relative reduction in proportion of calcium content in the $CaMn_3O_6$ catalyst from At% Mn:Ca of 3.10:1 to 3.87:1 after treatment in weak acidic for 10 min.

## Mass spectrometry analysis



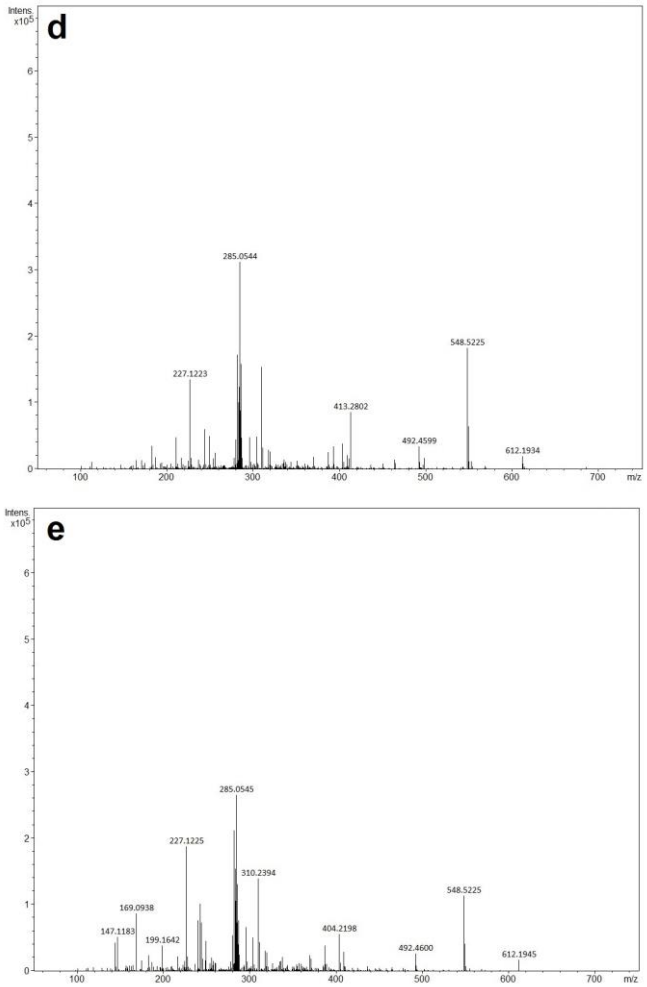



Fig. S3. Full scale mass spectrometry of photocatalytic reaction mixtures using $CaMn_3O_6$ catalyst, $[Ru(bpy)_3]^{2+}$ and $[Co(NH_3)_5Cl]Cl_2$ , before reaction (a) and after 60 min reaction using illumination of continuous or light cycled on:off(s) of (b) continuous; (c) 24:1.5(s:s); (d) 24:2(s:s); (e) 24:2.5(s:s). The pentamine cobalt electron acceptor is insoluble in the methanol MS carrier liquid, thus allowing clearer monitoring of $[Ru(bpy)_3]^{2+}$ and its relative decomposition.

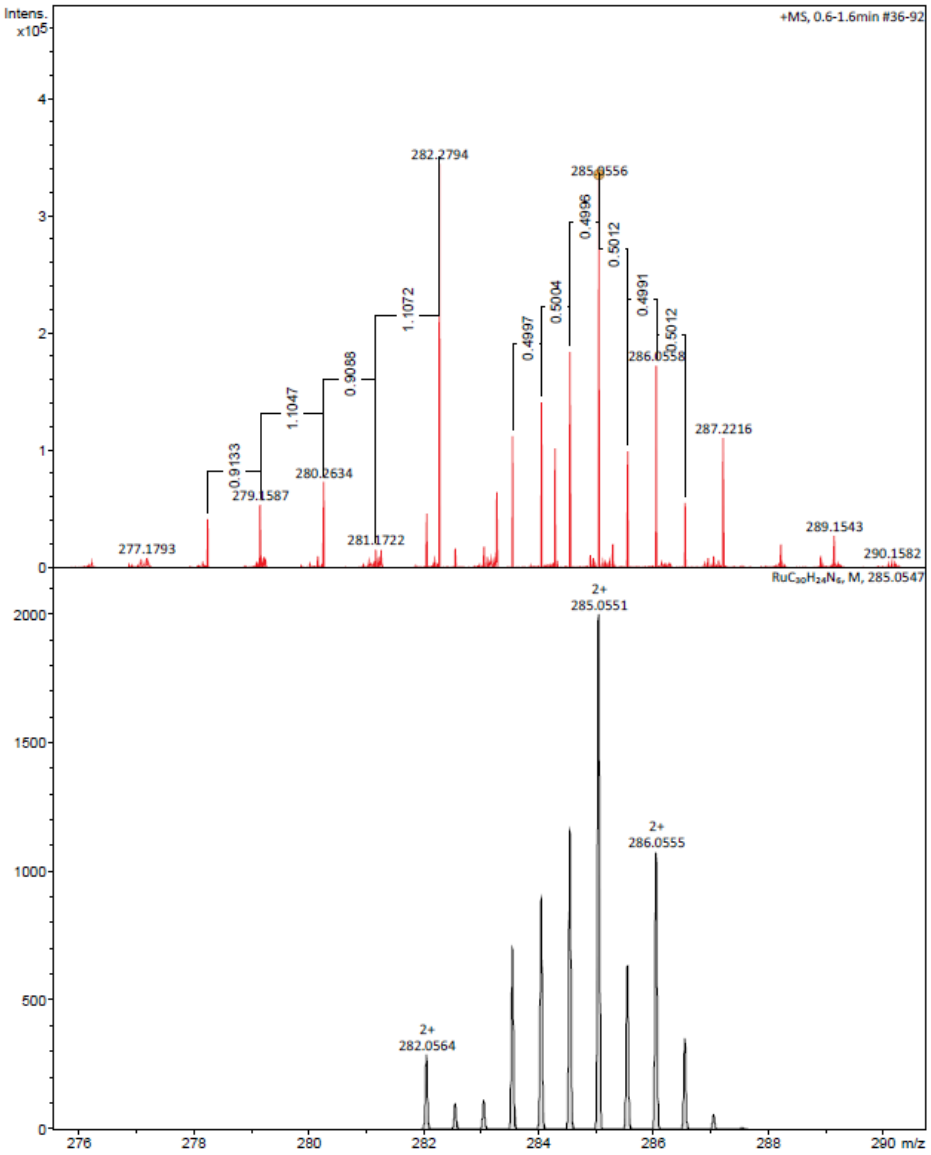



Fig. S4. Mass spectrometry of $[Ru(bpy)_3]^{2+}$ region of continuous illuminated $CaMn_3O_6$ reaction mixture after 60 min. reaction. The 0.5Da separation of the Ru isotopes confirms the z=2 charge on the ruthenium sensitizer at 285.055 and absence of ruthenium in the adjacent hydrocarbon fragment at m/z 282.279.

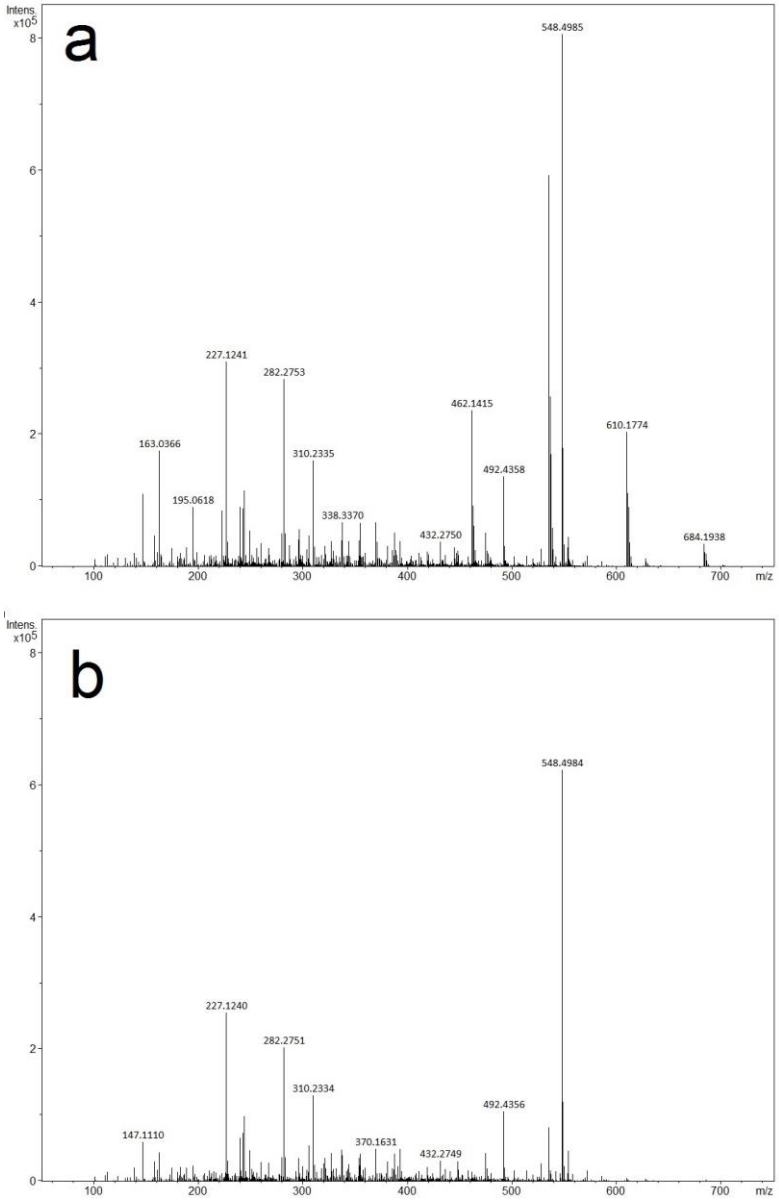



Fig. S5. Mass spectrometry of deposit accumulated on flask surface collected in methanol from 60min. photocatalytic reactions using $Fe_2O_3$ catalyst, $[Ru(bpy)_3]^{2+}$ and $[Co(NH_3)_5Cl]Cl_2$ using illumination of (a) continuous light; (b) 24:2(s:s) cycled on:off. An increased concentration and number of decomposed fragments were obtained using continuous light.

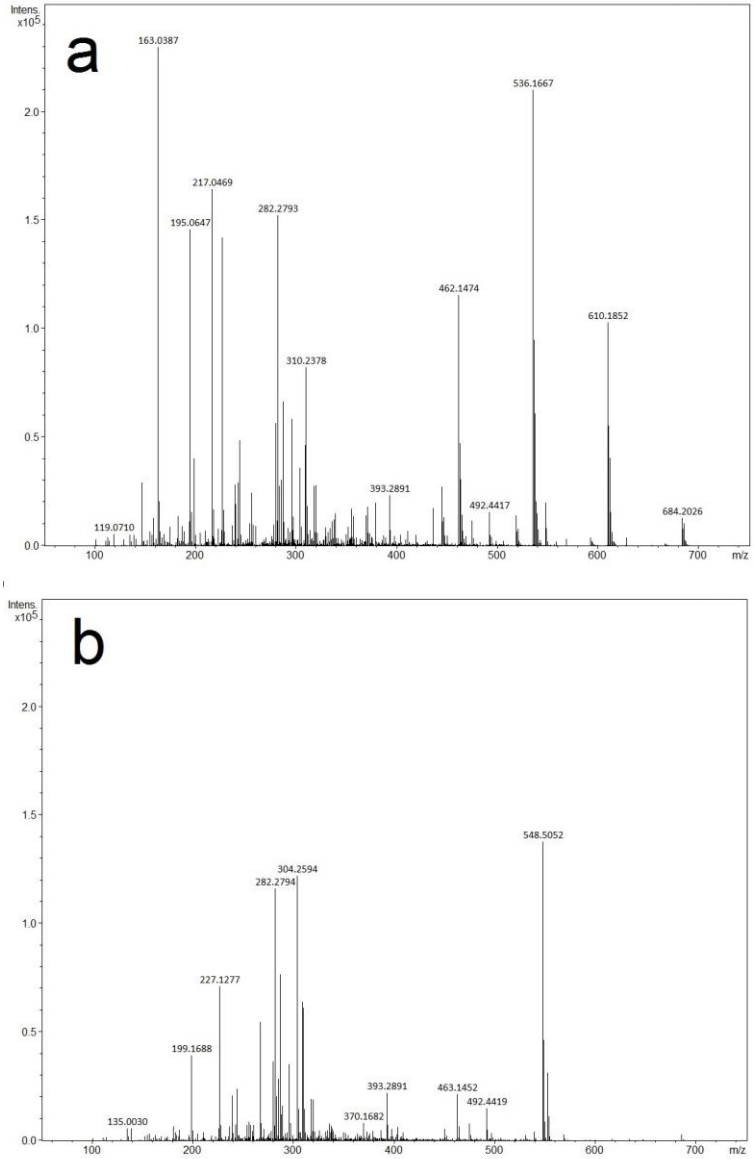



Fig. S6. Mass spectrometry of deposit accumulated on flask surface collected in methanol from 60mn. photocatalytic reactions using $Co_3O_4$ catalyst, $[Ru(bpy)_3]^{2+}$ and $[Co(NH_3)_5Cl]Cl_2$ using illumination of (a) continuous light; (b) 24:2(s:s) cycled on:off. An increased concentration and number of decomposed fragments were obtained using continuous light.

**Low reagent volume continuous flow system photocatalytic water oxidation**

**Methodology**

The reagent mixture was introduced into the flow set-up *via* a SF-10 low pulsation peristaltic pump (kindly donated by Vapourtec) at a rate of 450 µl/min and segmented by air/carrier fluid (delivered by a Syrris Asia dual-syringe pump, 300 µl/min) at a PP t-piece (thruhole 1.5 mm). 60 cm (length exposed to light) of 1.5 mm ID (internal diameter) fluorinated ethylene propylene (FEP) tubing, was coiled (9.3 cm diameter) and placed in a horizontal arrangement at a distance of 51.4 mm away from the light source such that blue led light at a measured 5mWcm$^2$ reached the coiled tube surfaces. Lighting using continuous illumination, or 24:2(s:s) or 0.06:0.005(s:s) on:off cycled repeatedly during light on periods. The flow rate of 750 µl/min of the combined flow was kept constant throughout all experimental runs producing a residence time (RT) of 1 min 58 s. The reaction mixture only component residence volume (RV) of the illuminated section was 0.7 ml with an average slug volume of 0.022ml.

In order to measure the oxygen content of the system and ensure suspension of the solid catalyst, air-segmentation was employed. Custom flow cells for on-line pH and $O_2$ analysis were designed to minimise dead volume, maximising responsivity of the analysis to changes in environment. pH and $O_2$ were measured using the same instrumentation as with the batch reaction system. The flow system rig is shown in Fig. S7. The coiled sections of tubing containing the flowing reaction mixture subjected to blue led illumination are shown in Fig. S8. a,b.

A control experiment using 0.005:0.06(s:s) on:off cycled during light on periods was also conducted, which resulted in no measurable $O_2$ generation and negligible pH rise to 5.4 after 10 min. reaction time.

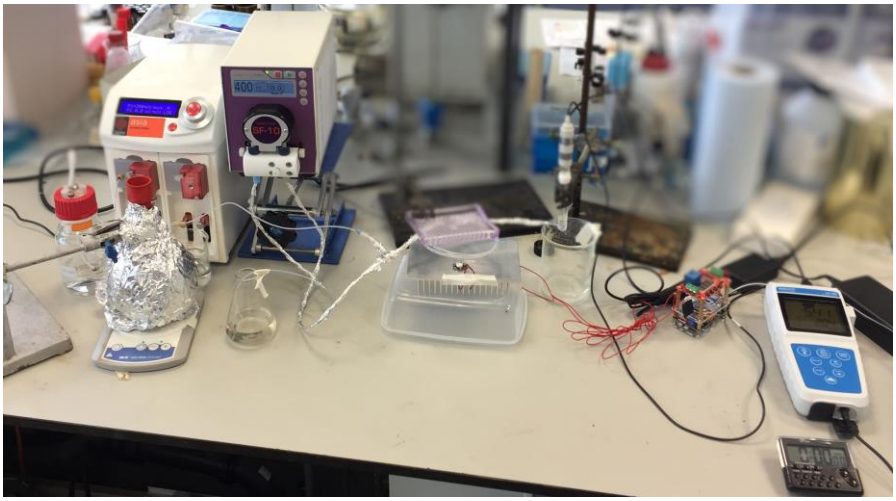


Fig. S7. Image of continuous flow system for photocatalytic water oxidation using oxidations using 0.45g$[Ru(bpy)_3]^{2+}$, 1.25g$[Co(NH_3)_5Cl]Cl_2$ and 0.1g $Co_3O_4$ catalyst in stirred 350ml of $N_2$ degassed 50mM acetate buffer at pH 5.2.

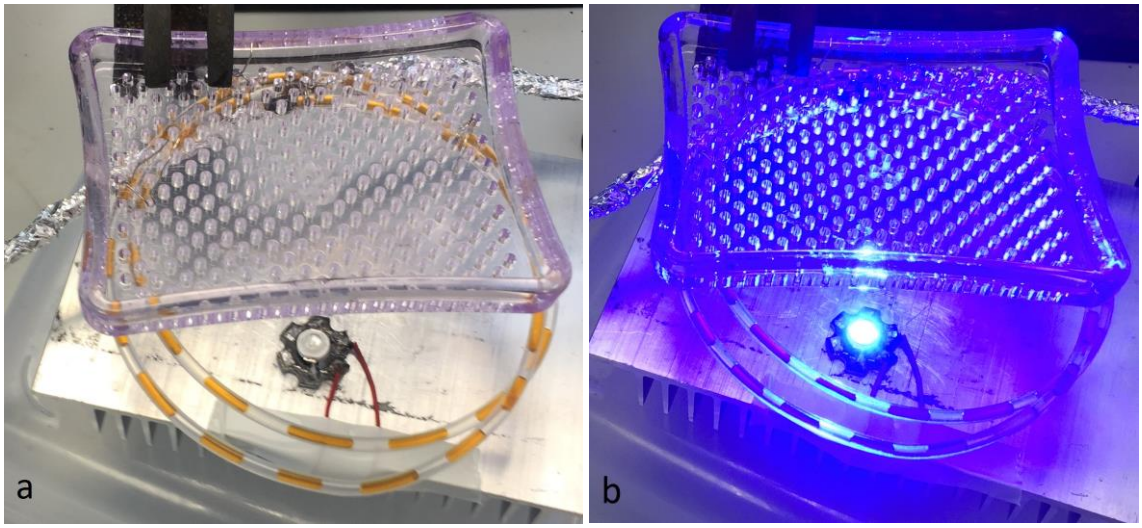



Fig. S8. Continuous flow system showing (a) 60cm of coiled section of FEP tubing with average of 0.022ml sections of reaction mixture pumped at rate of 750µl/ min; (b) coiled section under led illumination.

**Example calculations**

***Example of Turn over Frequency calculation***

Taking as example the prepared α-$Fe_2O_3$ sample in a photocatalytic reaction using continuous illumination

10mg of α/γ-$Fe_2O_3$ = 6.994mg of Fe present in photocatalytic reaction

Moles = 6.994mg/55.84 = 0.1252 x$10^{-3}$ moles

Measured maximum level of $O_2$ generation for t = 0 to 20min was 0.03023μmol per second

TOF = 0.03023μmol $sec^{-1}$ / 0.1252 x $10^{-3}$ moles = 0.2414 x $10^{-3}$ mol ($O_2$) $sec^{-1}$/ mol (Fe)

**TOF = 0.2414 x $10^{-3}$ $s^{-1}$ = 2.414 x $10^{-4}$ $s^{-1}$**

TOF's for other systems were determined similarly and were normalized to active metal present

***Example of Quantum Yield (Φ) calculations***

A photonic method was used for determining Quantum Yields, $O_2$ yields after 40min of reaction time were taken.

a) Taking as example the prepared α/γ-$Fe_2O_3$ sample using continuous illumination of 5mW$cm^{-2}$

b)Using wavelength of $\lambda_{max}$ absorption of $[Ru(bpy)_3]^{2+}$ in water of 454nm, intensity of light measured at 5mW$cm^{-2}$ impinging on 31.5$cm^2$ surface = 157.5mW, maximum $O_2$ yield obtained after 40 min used.

Energy of a single photon at 454nm = h.c/λ

= 6.626x$10^{-34}$ x 2.998 x $10^8$/ 454 x $10^{-9}$ = 4.375 x $10^{-19}$ J

Total power absorbed = 157.5mW x 40 min x 60 = 378J

Number of $O_2$ molecules produced = 51.6μmol x 6.022 x $10^{23}$ = 3.107x $10^{19}$

Taking that 4 photons are absorbed per $O_2$

**Quantum Yield Φ = 3.107 x$10^{19}$ / (378J/ 4.375 x $10^{-19}$ J) x 400% = 14.4%**

c) Taking as example the prepared α/γ-$Fe_2O_3$ sample using 24:2 on:off(s) timing

= 24/26 x 5mW$cm^{-2}$ = 4.615mW$cm^{-2}$ blue light illumination.

Using wavelength of $\lambda_{max}$ absorption of $[Ru(bpy)_3]^{2+}$ of 454nm in water, intensity of light measured at 4.615mW/$cm^{-2}$ impinging on 31.5$cm^2$ surface = 145.4mW, maximum $O_2$ yield obtained after 40 min used.

Energy of a single photon at 454nm = h.c/λ

= 6.626x$10^{-34}$ x 2.998 x $10^8$/ 454 x $10^{-9}$ = 4.375 x $10^{-19}$ J

Total power absorbed = 145.4mW x 40 min x 60 = 348.9J

Number of $O_2$ molecules produced = 116μmol x 6.022 x $10^{23}$ = 6.985 x $10^{19}$

Taking that 4 photons are absorbed per $O_2$

**Quantum Yield Φ = 6.985 x $10^{19}$ / (348.9 J/ 4.375 x $10^{-19}$ J) x 400% = 35%**

Quantum Yields for other systems were calculated similarly.

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