Electronic Supporting Information

Visible light promoted photocatalytic water oxidation: effect of fluctuating light intensity upon reaction efficiency

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Materials

Xyloglucan (MW~60K) was obtained from Dainippon Sumitomo Seiyaku, Co. Ltd., Osaka, Japan and was used as supplied. All other materials were obtained from Sigma-Aldrich Co. and used as supplied.

Experimental

Preparation of α-Fe_2O_3. 8g of $Fe(NO_3)_3.9H_2O$ (0.02mol) was dissolved in 75ml DI water, 3g of xyloglucan was then slowly added to the vigorously stirred mixture until it was fully dissolved and a viscous solution formed. This mixture was spread onto a large crystallizing dish allowed to fully dry to form as a thin film. Samples of the film were cut into slices and heated in a ceramic crucible to 500°C and a heating rate of 20°Cmin^{-1} and held at 500°C for 10 minutes. A controlled combustion of the material occurred at ~200-220°C and traces of remaining carbon removed on heating to 500°C. A red/orange powder was obtained which was analysed by X-ray diffraction and TEM microscopy. A commercial laser ablated Co_3O_4 (Sigma-Aldrich 637025, measured S_{BET} = 35.8m^2 g^{-1}) was also used for comparison in photocatalytic water oxidations.

Water oxidations

Nitrogen degassed DI water was used to prepare an acetate buffer of pH 5.1 (50mM sodium acetate adjusted with acetic acid). A custom made three arm 50ml glass flask was taken and 124 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 25ml 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 10ml of the degassed buffer was then added. The light shielded reaction flask was then left stirring for 10 minutes for the system to equilibrate. The light shield covering was then removed and the stirred flask illuminated by a 25W SL RGB Four Leafage Fiber, Shenzen Co. Ltd. in pure blue light mode (λ_{max} 455nm) held at a specific distance from the edge of the reaction flask to give a generated measured output of 5mWcm^{-2} (Solartech Inc. Solar Meter 9.4), at the reaction flask (with measured led light exposed surface area of 31.5cm^2). This light source has an RGB repeating cyclic colour changing output with adjustable cyclic timing and this source was employed for fluctuating lighting reactions, cycles of 100, 50 and 25 sec. duration before repeat of the same spectral cycle were used.

Finally, 3W Bridgelux-EPILED chip led's with λ_{max} emission of 410, 450 and 500nm and λ emission bands of 400-440, 410-470 and 470-540nm were also employed as a combined saturation illumination source. Light source distance to flask edge was adjusted such that intensity was measured at 5mWcm^{-2} at the reaction flask.

O_2 release was monitored in situ 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 fluctuation in reaction flask temperature. 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 = (124mg/250.4)/ 4 mol = 123.8μmol O_2.

During a photocatalyzed water oxidation the $[Co(NH_3)_5Cl]Cl_2$ electron acceptor decomposes with release of ammonia and $Co(OH)_2$.[1]

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

Control experiments

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 lag phase of over 8 min due some self-decomposition of the ruthenium dye sensitizer and its conversion into a weakly active catalyst. With a control experiment using degassed DI water in place of the 50mM acetate buffer it was found that after light-on pH of the reaction rapidly rose to above pH 9 and the reaction then rapidly shut-down due to apparent decomposition of the light sensitizer as the high pH.

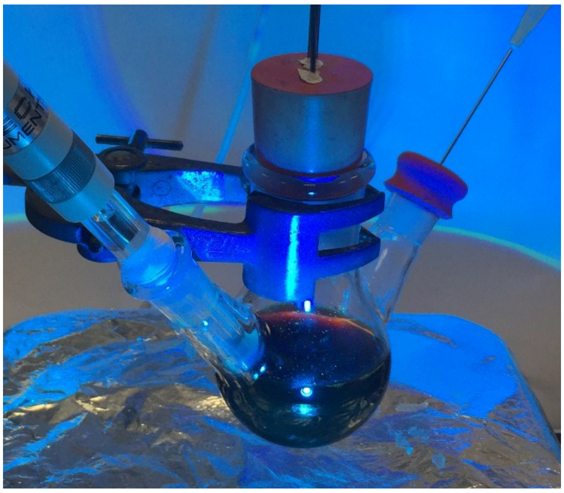

Image of reaction flask containing optical O_2 sensor and stirred reaction mixture with pH and temperature probe.

Instrumentation

Oxygen measurements

Accurate realtime gaseous O_2 generation into reaction flask headspace was determined with a Pyroscience Firesting O2 fibre optic oxygen meter fitted with an OXYROB10 robust O_2 probe coupled with a TDIP15 temperature compensation probe.

pH measurements

Realtime pH measurement was undertaken using a Eutech Cyberscan pH 450 with a pH and temperature probe held within the stirred reaction mixture. A USB output to a linked PC with CyberComm 450 V1.21 software used to record pH data.

TEM

Samples were sonicated in water and mounted on formvar coated copper mesh girds and examined using a Jeol 1200 EXII TEM operating at 120kV with attached digital camera.

Powder X-ray diffraction

Powder samples were analysed using a Bruker D8 powder X-ray diffractometer (CuKα) with a PSD LynxEye Detector.

UV/vis spectrometry

Solid state UV-vis reflectance spectrometry of powder samples over 320-800nm was conducted using a Perkin Elmer Lambda 750s UV/Vis/NIR spectrophotometer fitted with a Labsphere 60 mm integrating sphere. Background correction was made using a Labsphere certified reflectance standard

Emission spectra

Visible light emission spectra from light sources were measured using a Perkin-Elmer LS55 Luminescence Spectrometer in phosphorescence emission mode with the led lights directed via an optical fibre used in place of the spectrometer light source. WinLab Version 4.00.03 software via a linked PC was used for collecting data.

Surface area analysis (BET)

Calculated BET specific surface areas from gas sorption (N_2, 77 K) were measured on Micromeritics 3-Flex gas sorption analyser. Before the analysis, the sample was pre-degassed at 150 °C for 8 hours under vacuum (10^{-3} mbar) in an oven and then degassed at 200 °C for 12 hours under dynamic high vacuum (10^{-6} mbar).

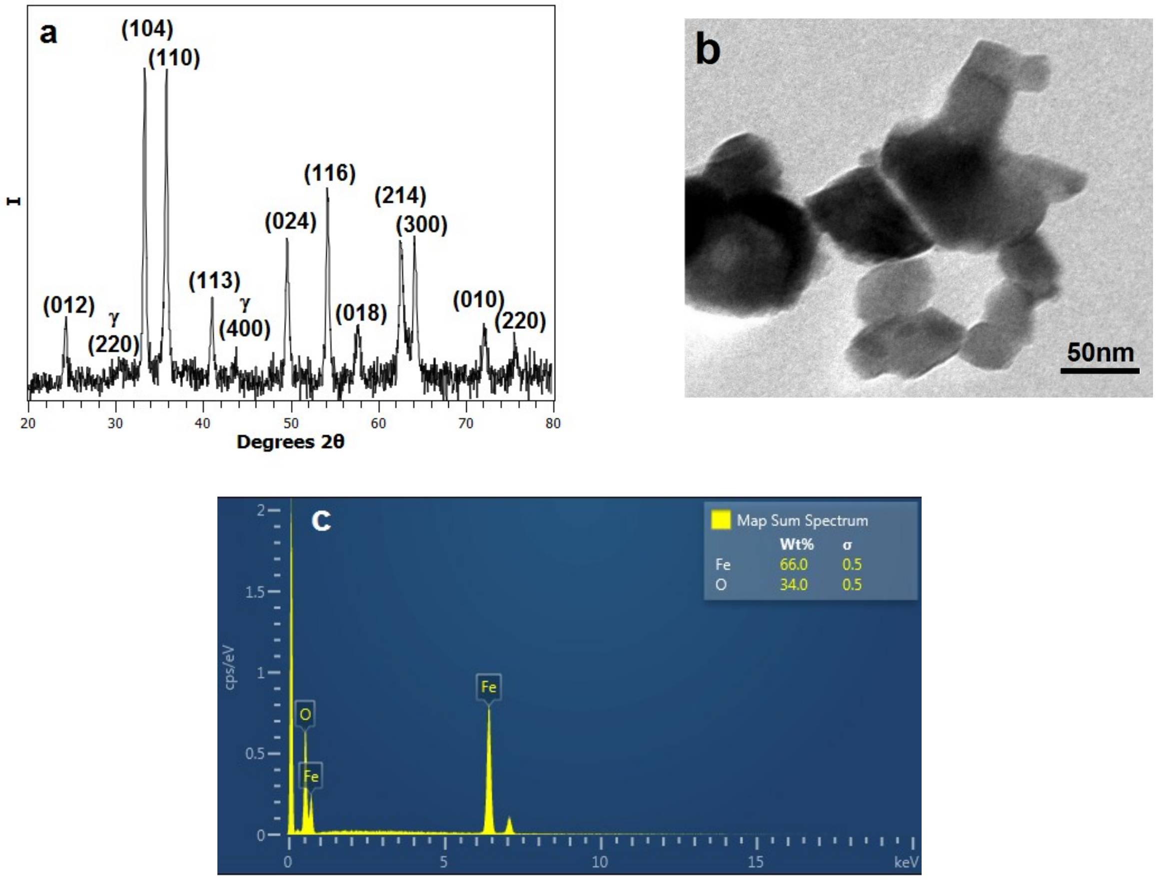

Fig.S1.(a) Powder XRD of α-Fe_2O_3 (JCPDS 013-0534, hematite) with trace level of γ-Fe_2O_3 (JCPDS 024-081, maghemite) prepared by calcination with xyloglucan used as a sacrificial size limiting biopolymer; (b) TEM image of the α-Fe_2O_3 nanoparticles; (c) EDX analysis of the Fe_2O_3 catalyst showing presence of iron and oxygen only.

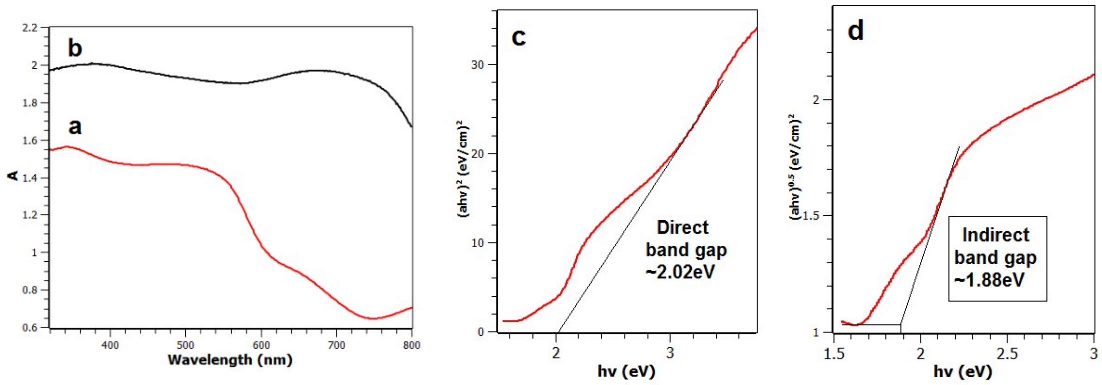

Fig. S2. Solid state UV-visible spectroscopy of catalysts showing (a) Fe_2O_3; (b) commercial Co_3O_4; (c) Tauc plot showing direct band gap of ~2.02eV of the Fe_2O_3 catalyst; (d) Tauc plot showing visible light indirect band gap of ~1.88eV of the Fe_2O_3 catalyst.

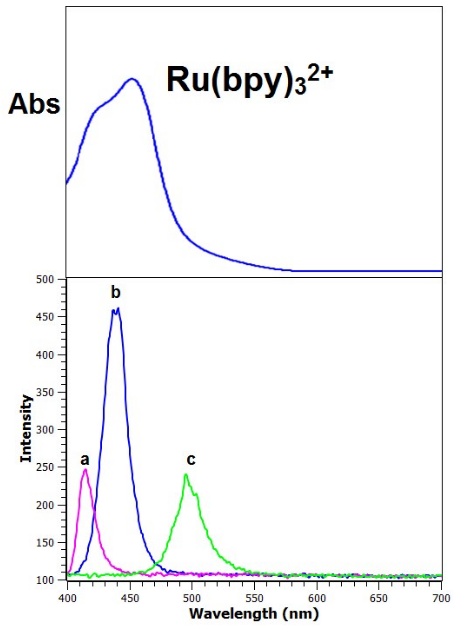

Fig. S3. Graph of measured relative intensity and wavelengths of led emissions used as combined $[Ru(bpy)_3]^{2+}$ saturation light source in photocatalytic water oxidation reactions showing (a) 410; (b) 450 and (c) 500 nm maximum wavelengths. The visible light absorption spectrum of $[Ru(bpy)_3]^{2+}$ is shown for comparison.

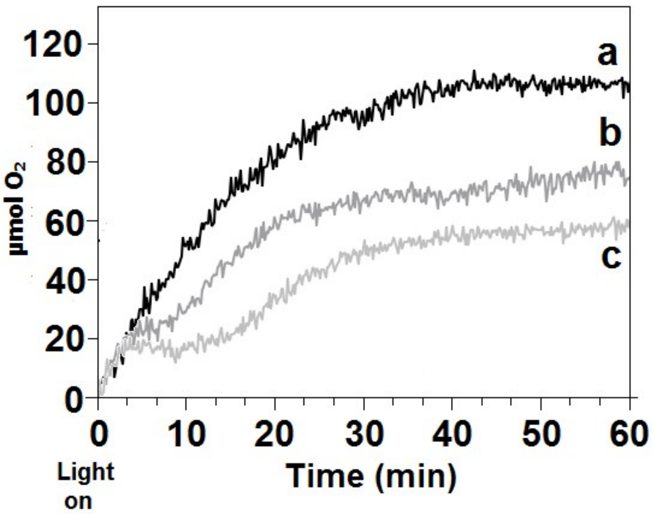

Fig. S4. Graph of released O_2 (μmol) against time for photocatalyzed water oxidation reactions with a α-Fe_2O_3 catalyst, reactions illuminated for 60min were conducted using a light source with a repeating wavelength/ intensity cycle of duration (a) 50s; (b) 25s; (c) 100s.

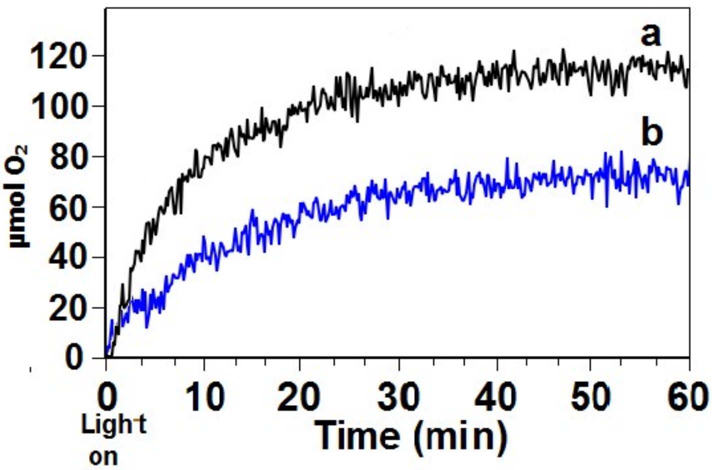

Fig.S5. Graph of released O_2 (μmol) against time for photocatalyzed water oxidation reactions with a Co_3O_4 catalyst using (a) repeating 50s cycle light source, $\bar{x}$ =3.3mWcm^{-2}; (b) blue light (λmax 455nm) @ 5mWcm^{-2}.

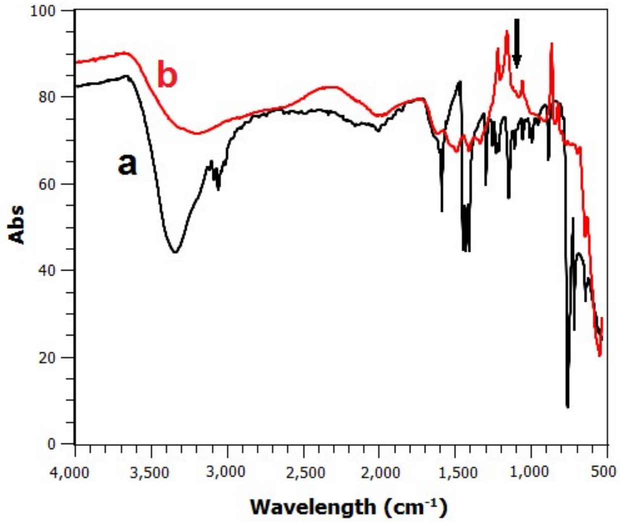

Fig. S6. Graph of FT-IR of (a) $[Ru(bpy)_3]Cl_2.6H_2O$; (b) low solubility decomposition material deposited during a photocatalytic water oxidation onto glass flask surface. The breakdown material was composed of bipyridine together with hydroxylated-$Ru(bpy)_2^{2+}$ derivatives as indicated by a prominent band at ~1120cm^{-1} (arrowed) which corresponds to a C-O(str).[2]

Example calculations

Example of Turn over Frequency calculation

Taking as example the prepared α-Fe_2O_3 sample

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

Moles = 6.994mg/55.84 = 0.1252 x10^{-3} moles

Measured maximum level of O_2 generation for t = 0 to 10min was 0.096μmol per second

TOF = 0.096μmol sec^{-1} / 0.1252 x 10^{-3} moles = 0.7668 x 10^{-3} mol (O_2) sec^{-1}/ mol (Fe)

TOF = 0.7668 x 10^{-3} s^{-1} = 7.668 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 reaction cessation after 40min were used.

a) Taking as example the prepared α-Fe_2O_3 sample using repeat 50s cyclic illumination of average 3.3mWcm^{-2}.

Using wavelength of λ_{max} absorption of $[Ru(bpy)_3]^{2+}$ of 454nm, intensity of light measured at 3.3mWcm^{-2} impinging on 31.5cm^2 surface = 103.95mW, maximum O_2 yield obtained after 40 min used.

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

= 6.626x10^{-34} x 2.998 x 10^8/ 454 x 10^{-9} = 4.375 x 10^{-19} J

Total power absorbed = 103.95mW x 40 min x 60 = 249.5J

Number of O_2 molecules produced = 108μmol x 6.022 x 10^{23} = 6.504 x 10^{19}

Taking that 4 photons are absorbed per O_2

Quantum Yield Φ = 6.504 x 10^{19} / (249.5 J/ 4.375 x 10^{-19} J) x 400% = 45.6%

b) Taking as example the prepared α-Fe_2O_3 sample using continuous 5mWcm^{-2} blue light illumination.

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

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

= 6.626x10^{-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 = 79μmol x 6.022 x 10^{23} = 4.757 x 10^{19}

Taking that 4 photons are absorbed per O_2

Quantum Yield Φ = 4.757 x 10^{19} / (378 J/ 4.375 x 10^{-19} J) x 400% = 22.0%

Quantum Yields for other systems were calculated similarly.

References

1. Duan, L., et al., *Visible Light-Driven Water Oxidation by a Molecular Ruthenium Catalyst in Homogeneous System.* Inorganic Chemistry, 2010. **49**(1): p. 209-215.

2. Vaidyalingam, A. and Dutta, P.K., *Analysis of the Photodecomposition Products of $Ru(bpy)_3^{2+}$ in Various Buffers and upon Zeolite Encapsulation*, Anal. Chem. 2000. **72**(21): p 5219-5224.