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 $\alpha$-Fe$_2$O$_3$. 8g of Fe(NO$_3$)$_3$.9H$_2$O (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$_3$O$_4$ (Sigma-Aldrich 637025, measured S$_{\text{BET}} = 35.8$ m$^2$ 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$_3$)$_5$Cl]Cl$_2$ electron acceptor and 45mg [Ru(bipy)$_3$]Cl$_2$.6H$_2$O (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 ($\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ emission of 410, 450 and 500nm and $\lambda$ 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).
O₂ production after light on was monitored for 60 minutes. Micromoles of O₂ gas released into the known headspace volume was calculated from measured O₂ 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 O₂ and proton release profiles shown. Maximum theoretical yield of O₂ based on electron acceptor concentration = (124mg/250.4)/ 4 mol = 123.8µmol O₂.

During a photocatalyzed water oxidation the [Co(NH₃)₅Cl]Cl₂ electron acceptor decomposes with release of ammonia and Co(OH)₂.[1]

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[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + [\text{Ru(bpy)}_3]^{2+} \rightarrow [\text{Ru(bpy)}_3]^{3+} + \text{Co}^{2+} + 5\text{NH}_3 + \text{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 O₂ 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 O₂ 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$_2$O$_3$ (JCPDS 013-0534, hematite) with trace level of γ-Fe$_2$O$_3$ (JCPDS 024-081, maghemite) prepared by calcination with xyloglucan used as a sacrificial size limiting biopolymer; (b) TEM image of the α-Fe$_2$O$_3$ nanoparticles; (c) EDX analysis of the Fe$_2$O$_3$ catalyst showing presence of iron and oxygen only.
Fig. S2. Solid state UV-visible spectroscopy of catalysts showing (a) Fe$_2$O$_3$; (b) commercial Co$_3$O$_4$; (c) Tauc plot showing direct band gap of ~2.02eV of the Fe$_2$O$_3$ catalyst; (d) Tauc plot showing visible light indirect band gap of ~1.88eV of the Fe$_2$O$_3$ 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 O₂ (µmol) against time for photocatalyzed water oxidation reactions with an α-Fe₂O₃ catalyst, reactions illuminated for 60 min were conducted using a light source with a repeating wavelength/ intensity cycle of duration (a) 50 s; (b) 25 s; (c) 100 s.

Fig. S5. Graph of released O₂ (µmol) against time for photocatalyzed water oxidation reactions with a Co₃O₄ catalyst using (a) repeating 50 s cycle light source, $\bar{X} = 3.3 \text{mWcm}^{-2}$; (b) blue light ($\lambda_{\text{max}}$ 455 nm) @ 5mWcm⁻².
Fig. S6. Graph of FT-IR of (a) [Ru(bpy)$_3$]Cl$_2$.6H$_2$O; (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 $\alpha$-Fe$_2$O$_3$ sample

$10$mg of $\alpha$-Fe$_2$O$_3$ = 6.994mg of Fe present in photocatalytic reaction

Moles = $\frac{6.994mg}{55.84}$ = $0.1252 \times 10^{-3}$ moles

Measured maximum level of O$_2$ generation for $t = 0$ to $10$min was $0.096\mu$mol per second

TOF = $0.096\mu$mol sec$^{-1}$ / $0.1252 \times 10^{-3}$ moles = $0.7668 \times 10^{-3}$ mol (O$_2$) sec$^{-1}$/ mol (Fe)

TOF = $0.7668 \times 10^{-3}$ s$^{-1}$ = $7.668 \times 10^{-4}$ s$^{-1}$

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

**Example of Quantum Yield ($\Phi$) 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 $\alpha$-Fe$_2$O$_3$ sample using repeat 50s cyclic illumination of average 3.3mWcm$^{-2}$.

Using wavelength of $\lambda_{max}$ 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 = $\frac{h.c}{\lambda}$

= $6.626 \times 10^{-34} \times 2.998 \times 10^{9} / 454 \times 10^{-9}$ = $4.375 \times 10^{-19}$ J
Total power absorbed = 103.95mW x 40 min x 60 = 249.5J
Number of O₂ molecules produced = 108μmol x 6.022 x 10²³ = 6.504 x 10¹⁹
Taking that 4 photons are absorbed per O₂
Quantum Yield Φ = 6.504 x 10¹⁹ / (249.5 J / 4.375 x 10⁻¹⁹ J) x 400% = 45.6%

b) Taking as example the prepared α-Fe₂O₃ sample using continuous 5mWcm⁻² blue light illumination.

Using wavelength of λmax absorption of [Ru(bpy)₃]²⁺ of 454nm, intensity of light measured at 5mW/cm⁻² impinging on 31.5cm² surface = 157.5mW, maximum O₂ yield obtained after 40 min used.

Energy of a single photon at 454nm = h.c/λ
= 6.626x10⁻³⁴ x 2.998 x 10⁸ / 454 x 10⁻⁹ = 4.375 x 10⁻¹⁹ J
Total power absorbed = 157.5mW x 40 min x 60 = 378J
Number of O₂ molecules produced = 79μmol x 6.022 x 10²³ = 4.757 x 10¹⁹
Taking that 4 photons are absorbed per O₂
Quantum Yield Φ = 4.757 x 10¹⁹ / (378 J / 4.375 x 10⁻¹⁹ J) x 400% = 22.0%

Quantum Yields for other systems were calculated similarly.

References