

Electronic Supporting Information

Visible light promoted photocatalytic water oxidation: effect of metal oxide catalyst composition and light intensity

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Experimental

Synthesis of metal oxides

For the synthesis of Co_3O_4 and Fe_2O_3 0.02M of the metal nitrate salt (3.65g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ respectively) was dissolved in 60ml of water in a flask held on a magnetic stirrer. For the synthesis of CoFe_2O_4 and MnFe_2O_4 0.0067M and 0.0133M of the corresponding metal nitrate salts were used. To this stirred solution 7.5g of dextran (Mr 70k) was added and dissolved with stirring. Dilute ammonia was added to raise the pH to 10.2 which was marked by a colour change to brown or black, the mixture was then stirred for a further 10min. before microwaving the solution briefly such that it was heated to 80°C , this was to assist in the formation of the spinel oxide. In the case of cobalt oxide preparations microwave heating was marked by a colour change from brown black to dark red. The mixtures were then cooled with ice and dilute nitric acid added dropwise to give a pH of ~ 8 , followed by centrifuging at 3500rpm for 10min to remove bulk precipitate. The supernatant solution was collected and dried in a fume hood followed by storing in a desiccator overnight.

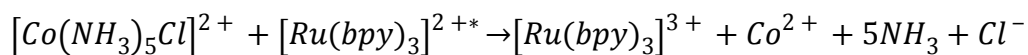
1-2g of the dried solid was then heated in ceramic crucible in a furnace to 450°C with a heating rate of 25°C min . It was observed a controlled combustion occurred between $170\text{-}220^\circ\text{C}$ with formation of high surface area open frameworks of metal oxide, heating was continued to 450°C and held at this temperature for 5 minutes to remove traces of residual carbon, before being allowed to cool to room temperature. Approximately 80mg of metal oxide per g of dried solid was obtained. A commercial laser ablated Co_3O_4 (Sigma-Aldrich 637025, measured $S_{\text{BET}} = 35.8\text{m}^2\text{ g}^{-1}$) was used for comparison.

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 120 mg of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (98%) electron acceptor and 45mg $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (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 20 minutes for the system to equilibrate. The light shield covering was then removed and the stirred flask illuminated by blue led (3W, 120 lumen, λ_{max} 455-465 nm) held at a specific distance from the edge of the reaction flask to give generated a measured output of between 0.6 to 10mW/cm^2 between 420-499nm (Solartech Inc. Solar Meter 9.4), at the reaction flask (with measured led light exposed surface area of 31.5cm^2). O_2 release was monitored in situ using a Pyroscience Firesting O_2 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 70 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 pH110 with an RS232 output. Samples runs were conducted in triplicate with representative O_2 and proton release profiles shown.

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

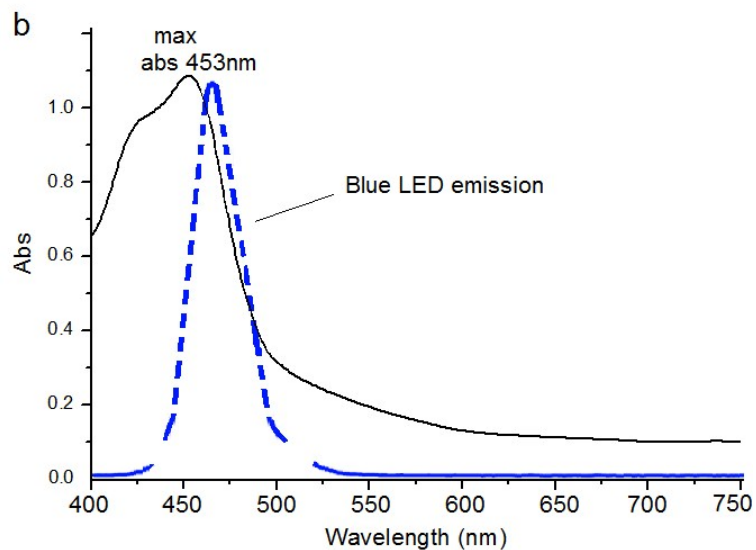


For experiments with repeat use of the mixed phase Fe_2O_3 , the catalyst was collected by use of a neodymium magnet followed by washing with DI water and drying before re-use in the reaction.

Photocatalytic water oxidations in the absence of $[Ru(bpy)_3]^{2+}$ or $[Co(NH_3)_5Cl]^{2+}$ gave no measurable O_2 production. Reactions conducted with $[Ru(bpy)_3]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$ in the absence of added metal oxide catalyst gave a low level production of $\sim 20 \mu\text{mol}$ of O_2 generation after 60 min following a prolonged lag time, most likely due to some in-situ generation of cobalt oxide from some decomposition of the pentamine electron acceptor.

a





a) Image showing photocatalytic water oxidation experimental set-up, a fibre optic O₂ sensor and temperature compensation probe were held in the flask head space, pH of the reaction was monitored simultaneously. Light at a measured mWcm⁻² intensity at the flask surface from a 455-465nm blue led was employed as the light source. (b) Visible light absorption spectrum of [Ru(bpy)₃]Cl₂ in degassed water and overlapping emission spectrum (dotted line) of the blue led illumination source.

Instrumentation

Oxygen measurements

Accurate gaseous O₂ was determined with a Pyroscience Firesting O2 fibre optic oxygen meter fitted with an OXYROB10 robust O₂ probe coupled with a TDIP15 temperature compensation probe.

SEM and Energy Dispersive X-ray analysis

FEG-SEM was conducted on uncoated samples using a JEOL JSM 6330F high resolution SEM fitted with a field emission gun. EDX analysis was conducted with an Oxford instruments ISIS 310.

Raman

Powder samples were analysed with a Bruker Equinox 55 spectrometer using a 532nm laser with an integrated FRA 106 Raman module.

TEM

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

Powder X-ray diffraction

Siemens D5000 powder X-ray diffractometer (CuK α)

UV/vis spectrometry

Solid state UV-vis reflectance spectrometry of powder samples over 250-800nm was conducted using a Perkin Elmer Lambda 750s UV/Vis/NIR spectrometer fitted with a Labsphere 60 mm integrating sphere. Background correction was made using a Labsphere certified reflectance standard.

Surface area analysis (BET)

Calculated BET specific surface areas from gas sorption (N₂, 77 K) were measured on Micromeritics 3-Flex gas sorption analyser. All samples were degassed at 150°C/8 h under dynamic high vacuum (10⁻⁶ mbar) prior to analysis.

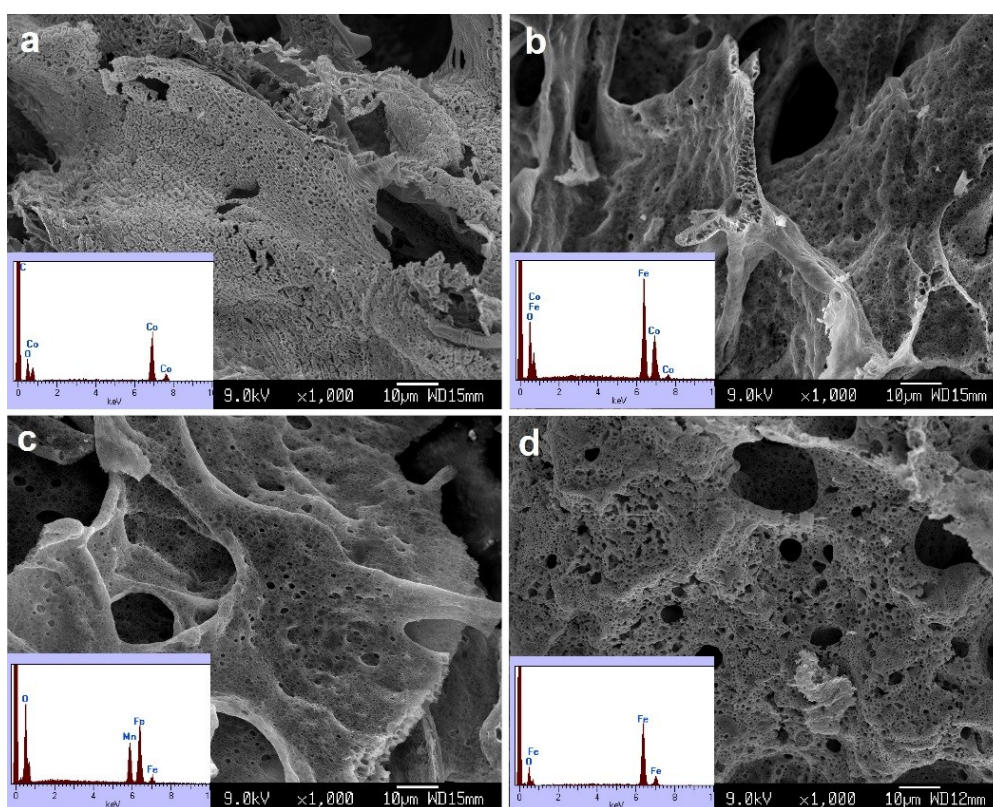
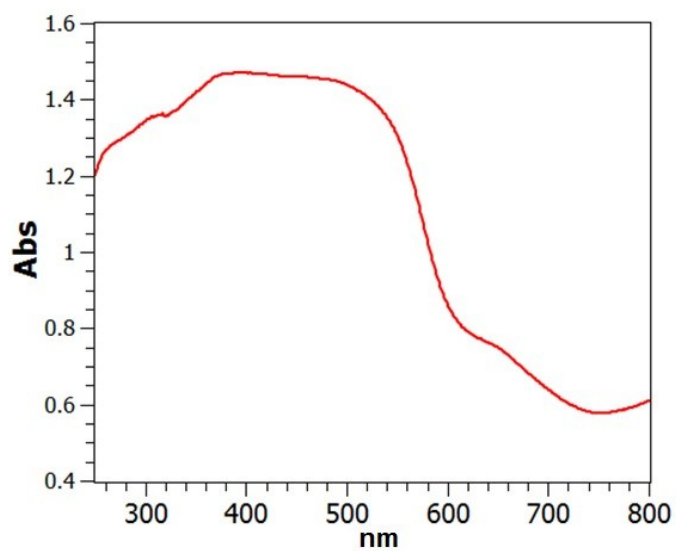


Fig. S1. SEM images of prepared samples of (a) Co_3O_4 ; (b) CoFe_2O_4 ; (c) MnFe_2O_4 ; (d) $\gamma/\alpha\text{-Fe}_2\text{O}_3$. Insets show measured EDX analysis.

a)



b)

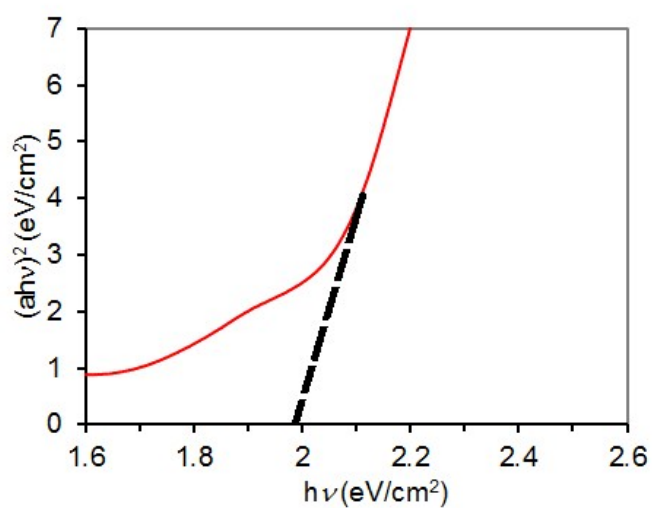


Fig. S2. (a) Solid state uv-visible spectrophotometry of prepared mixed phase Fe₂O₃; (b) Tauc plot of $(ah\nu)^2$ against $(h\nu)$ for the direct transition for Fe₂O₃ and extrapolation to $(ah\nu)^2 = 0$, which gives a band gap for this prepared mixed phase Fe₂O₃ of ~ 1.98 eV (626nm).

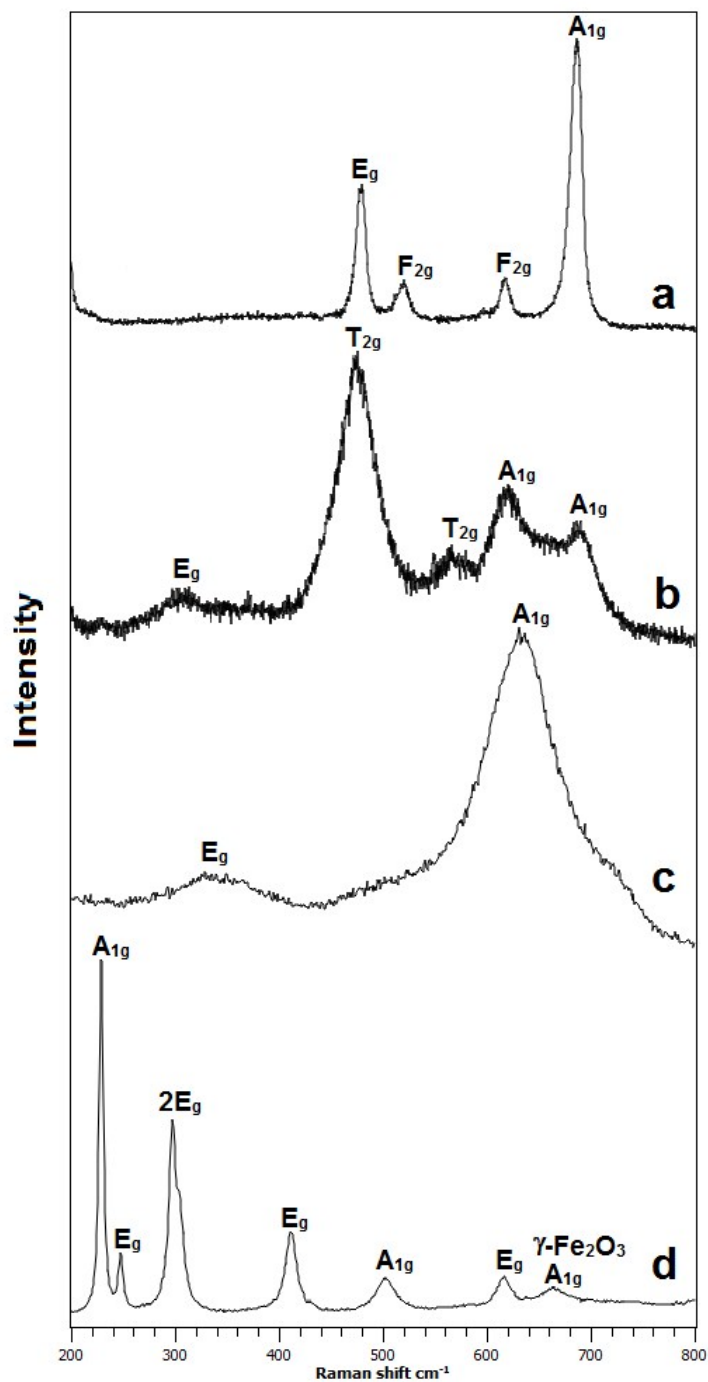


Fig. S3. Raman spectroscopy of prepared samples showing (a) Co_3O_4 ; (b) CoFe_2O_4 ; (c) MnFe_2O_4 ; (d) $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. Raman active phonon modes are labelled and correspond to reported shifts for the prepared samples. Raman intensities for $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) are weak therefore the spectrum is dominated by the $\alpha\text{-Fe}_2\text{O}_3$ (hematite) phase present.[2-5]

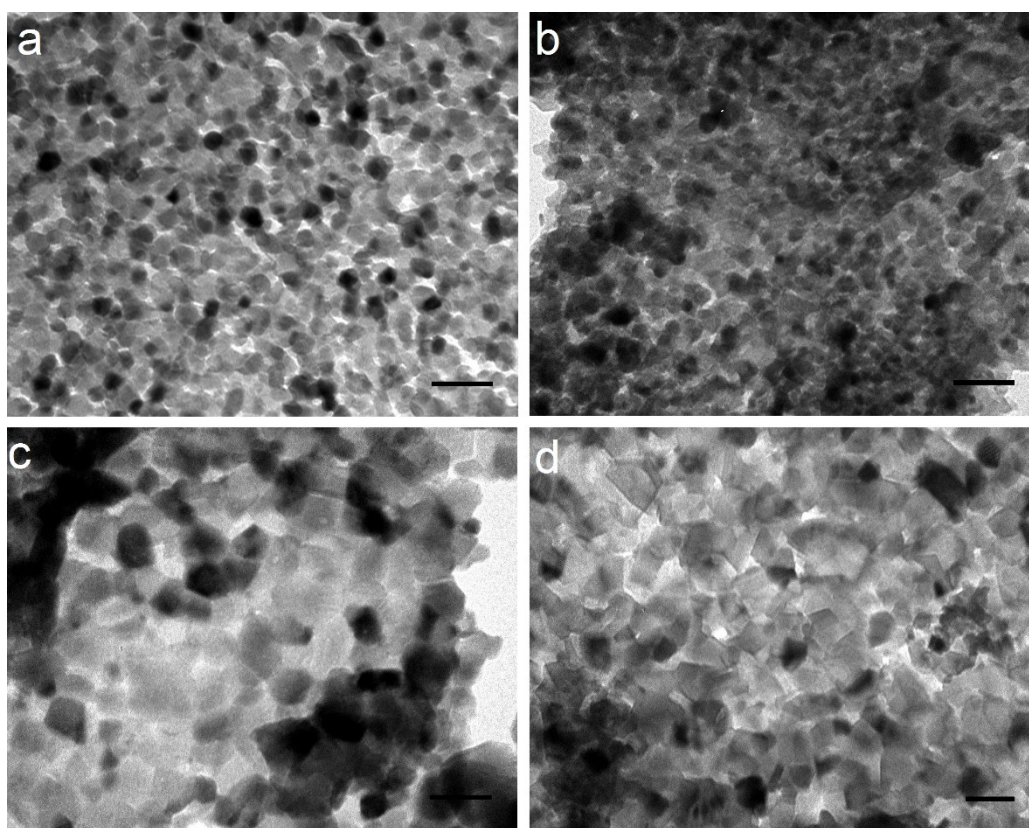


Fig. S4. TEM images of prepared metal oxides showing (a) Co_3O_4 ; (b) CoFe_2O_4 ; (c) MnFe_2O_4 ; (d) $\alpha/\gamma\text{-Fe}_2\text{O}_3$. Scale bar = 50nm.

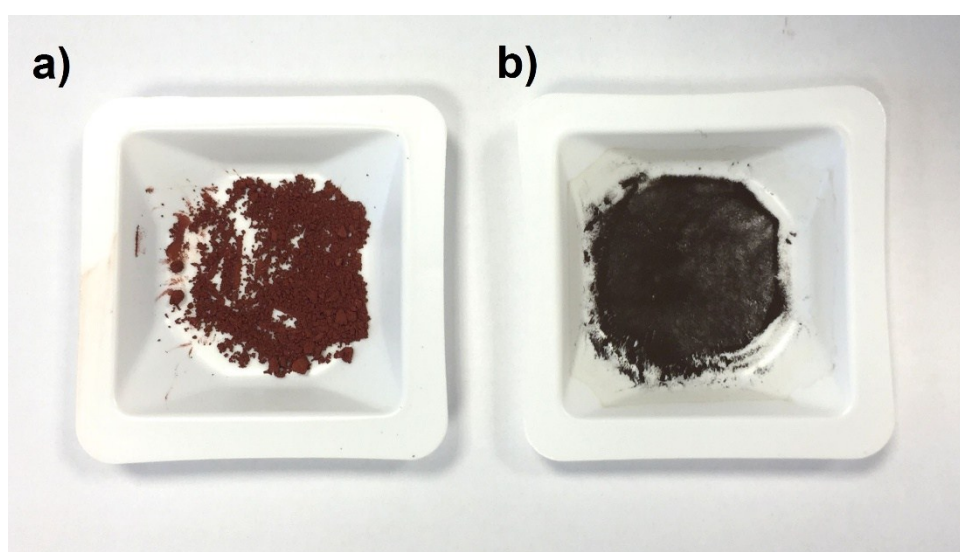
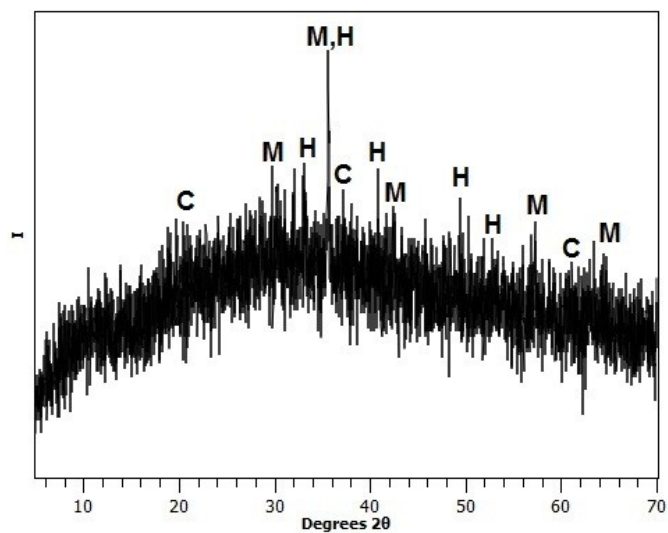


Fig. S5. Image of mixed phase Fe_2O_3 used as catalyst in photocatalytic water oxidation reaction (a) before reaction; (b) after four successive reactions showing darkening of colour due to surface accumulation of cobalt oxides from decomposed electron acceptor.

a)



b)

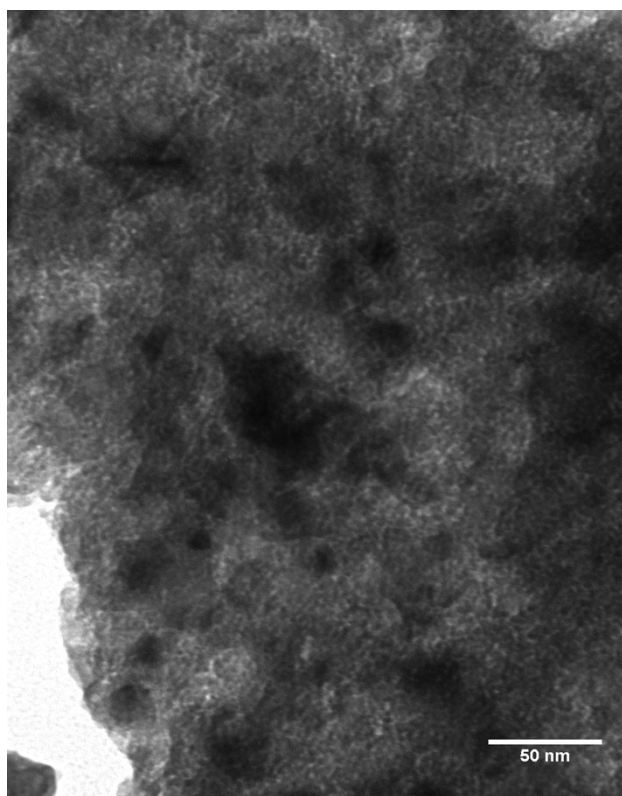


Fig. S6. Prepared mixed phase Fe_2O_3 catalyst after recovery from four successive photocatalytic water oxidation reactions (a) Powder XRD showing M-maghemite, H-hematite and C – Co_3O_4 ; (b) TEM image showing Fe_2O_3 crystals with bound coating of cobalt oxide nanoparticles after four successive water oxidation reactions.

Example calculations

Example of Turn over Frequency calculation

Taking as example the prepared Co_3O_4 sample

10mg of $\text{Co}_3\text{O}_4 = 7.342\text{mg}$ of Co present in photocatalytic reaction

Moles = $7.342\text{mg}/58.93 = 0.1245 \times 10^{-3}$ moles

Measured maximum level of O_2 generation was $0.105\mu\text{mol}$ per second

TOF = $0.105\mu\text{mol sec}^{-1} / 0.1245 \times 10^{-3}$ moles = 0.8433×10^{-3} mol (O_2) $\text{sec}^{-1} / \text{mol}$ (Co)

TOF = 0.843×10^{-3} mol (O_2) $\text{sec}^{-1} / \text{mol}$ (Co) (at the initial linear O_2 generation period)

TOF = $0.843 \times 10^{-3} \text{ s}^{-1}$

TOF's for other catalysts were determined similarly and were normalized to active metal or mixed metal content.

Example of Quantum Yield (Φ) calculation

Since the results showed that surface areas of the catalysts changed continuously throughout the reaction a photonic method was used for determining Quantum Yields.

Taking as example the prepared Co_3O_4 sample

Using wavelength of 452nm , intensity of light measured at $5\text{mW}/\text{cm}^2$ impinging on 31.5cm^2 surface = 157.5mW , maximum O_2 yield obtained within 35 min used.

Energy of a single photon at $452\text{nm} = h.c/\lambda$

= $6.626 \times 10^{-34} \times 2.998 \times 10^8 / 452 \times 10^{-9} = 4.365 \times 10^{-19} \text{ J}$

Total power absorbed = $157.5\text{mW} \times 35 \text{ min} \times 60 = 330.7\text{J}$

Number of O_2 molecules produced = $98\mu\text{mol} \times 6.022 \times 10^{23} = 5.901 \times 10^{19}$

Taking that 4 photons are absorbed per O_2

Quantum Yield $\Phi = 5.901 \times 10^{19} / (330.7 \text{ J} / 4.365 \times 10^{-19} \text{ J}) \times 400\% = 31.1\%$

Φ with other catalysts were calculated similarly taking into account maximum rate, yield and light intensity used.

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. Hadjiev, V.G., M.N. Iliev, and I.V. Vergilov, *The Raman spectra of Co_3O_4* . Journal of Physics C: Solid State Physics, 1988. **21**(7): p. L199.
3. Chandramohan, P., et al., *Cation distribution and particle size effect on Raman spectrum of CoFe_2O_4* . Journal of Solid State Chemistry, 2011. **184**(1): p. 89-96.

4. Pereira, C., et al., *Superparamagnetic MFe_2O_4 ($M = Fe, Co, Mn$) Nanoparticles: Tuning the Particle Size and Magnetic Properties through a Novel One-Step Coprecipitation Route*. Chemistry of Materials, 2012. **24**(8): p. 1496-1504.
5. El Mendili, Y., et al., *New evidences of in situ laser irradiation effects on γ - Fe_2O_3 nanoparticles: a Raman spectroscopic study*. Journal of Raman Spectroscopy, 2011. **42**(2): p. 239-242.