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Visible light promoted photocatalytic water oxidation: proton and electron collection via reversible redox dye mediator

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Visible light promoted photocatalytic water oxidations were conducted using a homogenous cobalt complex as a catalyst that was absorbed onto a silica gel substrate. The porous SiO_2 contained $Ru(bpy)_3^{2+}$ as light harvester and the redox quinone analogue DCPIP as a reversible electron mediator as a step towards utilization of protons and electrons liberated in water oxidations for solar fuels.

Sunlight is probably the leading alternative energy source available being plentiful, inexhaustible and safe. However electricity cannot be stored on the scale required and routes to solar fuels such as H_2 and methanol need to be developed using materials and methods applicable on a large scale.[1-3] In natural photosynthesis an inorganic $CaMn_4O_5$ arrangement evolved as a catalyst for the oxidation of water into gaseous O_2 and protons.[4] This ubiquitous cluster is housed within an elaborate supporting and regenerating oxygen evolving centre (OEC), itself contained within the plant chloroplast PSII complex. But it is worth noting that the manganese based structure may have evolved from a more primitive photosystem and that there are other metals equivalent or superior to manganese for the catalytic role that can be used in artificial systems. The artificial photocatalytic water oxidation reaction comprises (a) visible light, (b) a chemical light harvester, (b) a catalyst for dissociation of water molecules and (c) a sacrificial redox agent. For practical application many improvements need to be made in terms of efficiency, cost and toxicity of the reaction.[5]

The use of persulfate use as sacrificial electron acceptor has persisted since outset of studies of photocatalyzed water oxidations in the 1980s; however the powerful sulphate anion radical is generated which decomposes organics, generates CO_2 and limits reaction lifetime. A pentamine cobalt complex acceptor has also been employed widely, however this was demonstrated in our previous work and in the literature as potentially acting as a secondary catalyst following conversion *in-situ*.[6-8] Whilst catalyst and electron acceptor working in tandem can improve yields, the ultimate aim is to dispense with irreversible electron acceptors and utilize the protons and electrons for reductions into fuels. The use of an alternate electron mediator has clear benefits in developing this technology. Here we report the use of the redox quinone analogue 2,6-dichlorophenoindophenol (DCPIP) as a reversible electron mediator for collection of protons and electrons generated in an artificial photocatalyzed water dissociation. The successful viability of using a range of quinones or other agents such as polyamines as an electron collector with $Ru(bpy)_3^{2+*}$ has been reported.[9-11]

Under basic conditions DCPIP has an intense blue colouration (Abs λmax = 590nm) which converts to colourless upon reduction and protonation (Fig. 1 and ESI† Fig. S1). The Hill reaction using extracts from plant leaves has utilized this reagent extensively,[12, 13] however its use in fully artificial water oxidations systems has not been investigated. Here the DCPIP plays an equivalent role to $NADP^+$.[14, 15] Partially reduced DCPIPH is pink, further reduction gives colourless DCPIPH2 which is equivalent to $NADPH+H^+$ produced by light dependant photosynthesis PSII/PSI and can potentially be used as a synthetic proton/electron storage molecule.

Fig. 1 The redox indicator DCPIP (as sodium salt) is able to reversibly accept 2 protons and 2 electrons to form at DCPIPH2, onset of loss of the intense blue colouration occurs at ~pH 6.5 with formation of reduced pink DCPIPH then colourless DCPIPH2.

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† Electronic Supplementary Information (ESI) available: Experimental Details, TGA/DTA, BET, IR, XPS fluorescence data and TOF calculations are shown. See DOI: 10.1039/x0xx00000x

$Ru(bpy)_3^{2+}$ and DCPIP can be incorporated into silica sol-gels which facilitates its recovery and re-use in reactions (see ESI for experimental details).[16] BET measurements of lightly ground samples gave a surface area of ~348m²/g (BJH average pore diameter of ~41Å), the isotherm plot consistent with a micro/mesoporous material is shown in ESI† Fig. S2.

A soluble cobalt hydroxide-amino complex as catalyst was developed as a homogeneous catalyst to optimize interaction between the supported reagents. TGA and DTA analysis showed the sample was largely decomposed upon heating to 320°C, a partially reduced CoO/Co residue was formed. Residual mass after removal of absorbed water was ~40wt%. This is consistent with a $Co(OH)_x(NH3)_{(6-x)}$ sample (ESI† Fig. S3). FT-IR analysis showed strong absorption bands at 655cm^{-1} due to Co-OH vibrations and weak $Co\text{-}NH_{3(sym)}$ deformation bands at 1340 and 1400 together with water OH bands at 1630 and 3375cm^{-1} (ESI† Fig. S4).[17] This suggests the six-coordinate Co is primarily ligated by OH with minimal NH_3. In previous work more elaborate cobalt complexes were able to catalyse photo-oxidations.[6]

Stirred photocatalytic water oxidations were illuminated with a 3W blue LED (λ max 465 nm) held at a calibrated distance such that light intensity at the flask surface was 5mWcm^{-2}. Initial evaluations of the soluble cobalt complex catalyst activity were undertaken using a standard procedure with $[Ru(bpy)_3Cl]Cl_2$ sensitizer (MLCT absorbance maximum λ_{453nm}) and $[Co(NH_3)_5Cl]$ as electron acceptor in N_2 degassed DI acetate buffer at pH 5.2. For reactions utilizing the reversible electron mediator, 2.5g of lightly ground SiO_2 containing the $Ru(bpy)_3^{2+}$ sensitizer and DCPIP together with cobalt complex added in solution and of N_2 degassed DI water with pH adjusted to 7.2 with dilute NH_4OH was used. Following one reaction the SiO_2 gel powder was retrieved by filtration, washed, carefully degassed and DCPIP regenerated in highly dilute degassed ammonia at pH 7.2 before reuse. The release of O_2 and reaction mixture pH were monitored simultaneously in situ and in real time. An optical O_2 sensor combined with a temperature compensation probe was used for accurate measurement of gaseous O_2 released into the headspace (full experimental details are described in the ESI†).

Photocatalytic water oxidations using cobalt complex

Standard reactions to test activity of the soluble cobalt hydroxide complex as a homogenous catalyst showed that a total of ~90μmol of O_2 was evolved after 75 min of reaction time. This gives an efficiency of 75% based on a maximum yield of 120μmol due to electron acceptor concentration.[6] Calculated TOF for initial highest reaction rate was 0.28 X 10^{-3} s^{-1} (See ESI† for details of calculations). pH of the system rose from 5.2 up to 8.5 due to gradual decomposition of electron acceptor and generation of ammonia upon electron capture from the excited state $Ru(bpy)_3^{2+*}$.[18] The pentamine cobalt electron acceptor itself can contribute to O_2 and proton generation due to in-situ conversion into cobalt oxide.[6-7] This process was believed to become significant after approximately 40min reaction time and may account for the upswing in O_2 generation at around this point. This suggests O_2 evolved solely due to conversion of the cobalt complex to active Co^{3+} was ~60μmol (Fig. 2a,b), the additional O_2 being generated from cobalt oxide derived from both cobalt complexes.

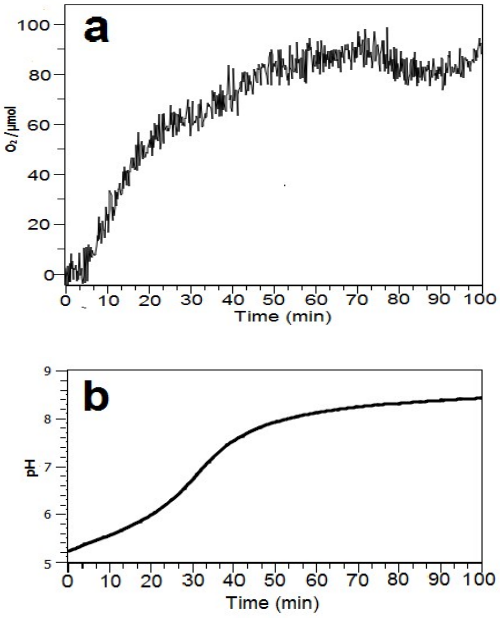


Fig. 2 (a) Visible light photocatalysed water oxidations showing O_2 yield with time using 5mWcm^{-2} blue light using 20mg of prepared $Co(OH)(NH_3)$ complex as homogeneous catalyst; (b) change in pH of the reaction mixture with time.

Photocatalytic reactions using DCPIP as electron mediator

Reactions using DCPIP in solution resulted in no measurable O_2 generation, presumably due to the intense deep blue coloured DCPIP blocking most incoming light. Previously, silica catalyst supports have been employed widely.[19,20] However, sol gels prepared incorporating $Ru(bpy)_3^{2+}$, DCPIP and soluble cobalt complex catalyst and were not active. However activity was obtained when the cobalt complex was firstly absorbed in a stirred photo reaction onto SiO_2-DCPIP-$Ru(bpy)^{2+}$ gels and then a further photocatalytic reaction undertaken using the recovered and washed combined $SiO_2/Ru(bpy)_3^{2+}/DCPIP/Co^{2+/3+}$ gel composite. Fig. 3 shows evolution of O_2 after light-on using this in-situ generated silica supported reagent mixture. It is worth noting that prior careful degassing to remove air from the combined SiO_2 microporous gel, which would otherwise quench the light generated $Ru(bpy)_3^{2+*}$ state, was required for its successful use in the photocatalytic reactions (see ESI† for experimental details).

After 30 min of reaction a maximum O_2 yield of ~54μmol was obtained. Calculated TOF was 0.179 x 10^{-3} s^{-1} (See ESI†). Activity and reaction lifetime was reduced compared to the homogeneous catalysed system, in part because of the absence of the pentamine electron acceptor conversion to active catalyst during later stages of the reaction. The SiO_2 gel with incorporated reagents was then recovered by filtration, washed and degassed and used in a further photocatalytic reaction. After 30 min a reduced O_2 yield of ~38μmol of O_2 was obtained. The reduction in activity of the silica gel supported mixture was

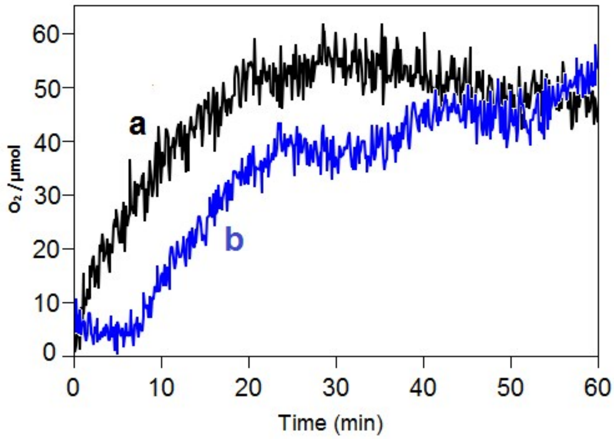


Fig.3 Visible light photocatalyzed water oxidations showing O_2 yield with time using $5mWcm^{-2}$ blue light with (a) SiO_2 support containing $Ru(bpy)_3^{2+}$ and DCPIP with cobalt complex post absorbed; (b) repeat reaction using recovered, washed and degassed SiO_2 support with its incorporated reagents.

probably due to degradation and some leaching of reagents into the reaction solution. The measured pH of the reaction mixtures remained almost unchanged, indicating collection of protons by the DCPIP.

Furthermore, it was observed that the SiO_2-DCPIP-$Ru(bpy)_3^{2+}$ with absorbed cobalt complex changed from a deep blue colour due to oxidized DCPIP into a red/orange colour. This was likely due to formation of reduced DCPIPH and DCPIPH2 which allowed the red/orange colour of this, the $Ru(bpy)_3^{2+}$ and the cobalt complex to become visible (Fig. 4).

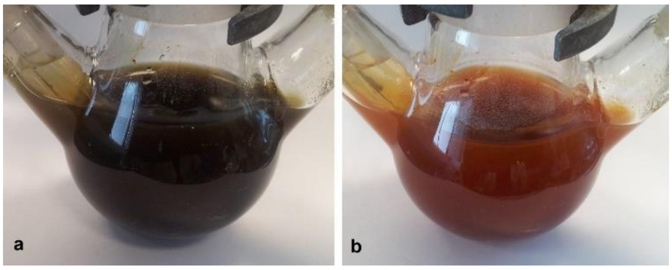


Fig. 4 Images of photocatalytic water oxidation reaction mixture using SiO_2 gel containing both $Ru(bpy)_3$ and DCPIP and Co complex in solution; (a) reaction mixture before exposure to blue LED light; (b) after exposure to the blue LED light for 100 min.

XPS analysis was used to determine the elemental composition of the catalyst, this showed the presence of Ru and also Co in SiO_2 support (ESI† Fig. S5). The Co 2p binding energy region showed the presence of mainly Co^{2+}, with $2p_{3/2}$ and $2p_{1/2}$ bands at 782 and 798eV respectively. A 3d-4s shake up was present at 787eV, also a small satellite peak situated at ~790eV was indicative of a low level of Co^{3+} due to Co_3O_4 (Fig. 5).[21-23]

Table 1 shows the composition of the generated SiO_2 catalyst mixture as measured by XPS. This showed that 2.5g of ground material had ~25mg of absorbed $Co(OH)_2/Co_3O_4$ and contained ~50mg of $[Ru(bpy)_3Cl]Cl_2$, though not all of this would be accessible for reaction.

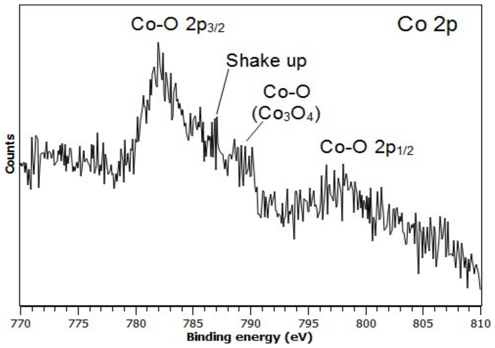


Fig. 5 High resolution XPS analysis of a washed sample of $SiO_2/Ru(bpy)_3^{2+}$/DCPIP following a photocatalytic reaction with homogeneous cobalt complex as catalyst. The Co2p region has band position and shape consistent with Co^{2+} together with small bands consistent with cobalt oxide as Co_3O_4. This shows the cobalt complex was absorbed onto the SiO_2 support and partly oxidized in-situ.

A simple further test using a solution of 20% hydrogen peroxide to confirm presence of cobalt ions was conducted. Ground SiO_2 prepared with $Ru(bpy)_3^{2+}$ and DCPIP showed no reaction upon addition to H_2O_2 solution. Significantly however, rapid and abundant H_2O_2 decomposition with generation of O_2 bubbles occurred with a washed SiO2/$Ru(bpy)_3^{2+}$/DCPIP retrieved following a photocatalytic reaction with cobalt complex in solution as catalyst.

Table 1 XPS analysis showing measured atomic and weight % of elements present in washed sample of $SiO_2/Ru(bpy)_3^{2+}$/DCPIP obtained following a photocatalytic reaction using the soluble cobalt complex as catalyst.

Element	At% (Wt%)	Element	At% (Wt%)
C	4.8 (3.03)	Cl	0.1 (0.19)
N	0.4 (0.29)	Co	0.2 (0.62)
O	68.79 (57.77)	Ru	0.05 (0.27)
Si	25.66 (37.83)		

Fluorescence resulting from relaxation of electrons from the MLCT $Ru(bpy)_3^{2+*}$ excited state via intersystem crossing to a triplet state and subsequent Stokes shifted emission to ground state in the silica support samples was examined by illumination of the powder samples by blue led light. Fig. 6 and shows the emission at ~600nm from samples containing $Ru(bpy)_3$. Samples recovered after photocatalysis showed reduced fluorescence intensity, probably due to some leaching. Typical absorption/ fluorescence wavelengths were measured (ESI† Fig. S6).[24]

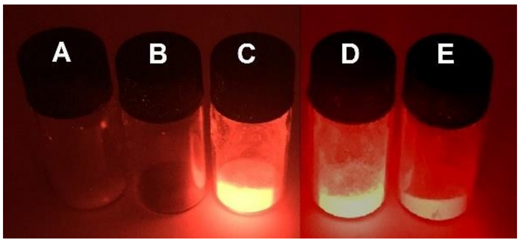
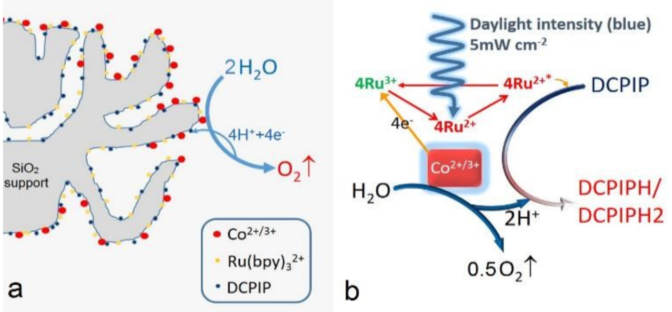


Fig. 6 Image of silica samples showing (a) SiO_2 only; (b) SiO_2- DCPIP; (c) SiO_2-$Ru(bpy)_3^{2+}$; (d) SiO_2-$Ru(bpy)_3^{2+}$-DCPIP; (e) SiO_2-$Ru(bpy)_3^{2+}$-DCPIP after one reaction in presence of Co^{2+}. (A blue light filter was used to show the yellow/orange emission).

Overall these results show the cobalt hydroxide-amino complex was adsorbed onto the SiO_2 substrate during the initial stirred photocatalytic reaction. The XPS results suggest some was converted to Co_3O_4 via excited state $Ru(bpy)_3^{2+*}$ electron extraction from Co^{2+} giving Co^{3+} without O_2 evolution. Thereafter $Co^{3+/4+}$ cycling and water oxidation occurs with generation of O_2 and protons:[6]

$$2H_2O + 4h\nu \rightarrow O_2\uparrow + 4H^+ + 4e^- \quad \text{(to DCPIP mediator)}$$

Exhaustion of the electron acceptor/ mediator leads to reduction and cessation of the reaction with time. Cessation using $Co(OH)_2$ and pentamine cobalt occurred gradually over 30-70 min as complex conversions into effective nano-cobalt oxide catalysts prolonged reaction at longer timescale.[6] With DCPIP, reaction cessation was abrupt after ~30 min since there were no such conversions into reaction generated catalysts. The suggested processes involved in water oxidation with the combined silica support are shown in Scheme 1a,b.



Scheme 1. (a) Microporous silica support containing $Ru(bpy)_3^{2+}$ light harvester and DCPIP as electron mediator and proton capture molecule with cobalt catalyst post absorbed to the support surface; (b) photocatalyzed water oxidation processes at silica support surface. Electrons and protons are captured by the DCPIP which is reduced and O_2 gas by-product liberated.

Conclusions

These experiments have shown that porous SiO_2 can be used as a reusable support for the $Ru(bpy)_3^{2+}$ light harvester and DCPIP as electron mediator for visible light promoted water oxidations. Degassing of the silica supports and post absorption of cobalt complex to the silica outer surface was found necessary to avoid likely quenching of the $Ru(bpy)_3^{2+*}$ excited state by oxygen in air and generated by the water oxidation. The DCPIP was found to function as an example reversible redox storage molecule and signifies possible future routes to utilization of electrons and protons released, e.g. by catalytic enzymes, for solar fuel production. Further work on utilizing alternative electron mediators and significantly increasing TOF's by optimizing reaction conditions is currently underway.

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Use of a quinone analogue as an example reversible electron and proton collector in visible light promoted water oxidations was investigated using reagents incorporated in microporous silica combined with a surface absorbed cobalt catalyst. Reversible storage molecules form an important step towards solar fuel production.