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)$_3$ 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. In natural photosynthesis an inorganic CaMn$_2$O$_5$ arrangement evolved as a catalyst for the oxidation of water into gaseous O$_2$ and protons. 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.

The use of persulfate as sacrificial electron acceptor has persisted since out 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 radical is generated which decomposes organics, generates CO and 2 electrons to form at DCPIPH$_2$, onset of loss of the intense blue colouration occurs at $\sim$pH 6.5 with formation of reduced pink DCPIPH then colourless DCPIPH2.

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

A soluble cobalt hydroxide-amo-no complex as catalyst was developed as a homogenous catalyst to optimize interaction between the supported reagents. TGA and DTA analysis showed the sample was largely decomposed upon heating to 320$^\circ$C, a partially reduced CoO/Co residue was formed. Residual mass after removal of absorbed water was $\sim$40wt%. This is consistent with a Co(OH)$_2$(NH$_3$)$_2$ as sample [ESI† Fig. S3]. FT-IR analysis showed strong absorption bands at 655 cm$^{-1}$ due to Co-OH vibrations and weak Co-NH$_2$(sym) deformation bands at 1340 and 1400 together with water OH bands at 1630 and 3375 cm$^{-1}$ (ESI† Fig. S4). 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.

Stirred photocatalytic water oxidations were illuminated with a 3W blue LED ($\lambda$ 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)$_3$Cl]$_2$ sensitizer (MLCT absorbance maximum $\lambda_{max}$=530nm) and [Co(NH$_3$)$_2$Cl] 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)$_3$Cl$_2$ 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$_2$OH 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 O₂ and reaction mixture pH were monitored simultaneously in situ and in real time. An optical O₂ sensor combined with a temperature compensation probe was used for accurate measurement of gaseous O₂ 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 O₂ 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 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)₂⁺₃⁺. The pentamine electron acceptor itself can contribute to O₂ 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 O₂ generation at around this point. This suggests O₂ evolved solely due to conversion of the cobalt complex to active Co³⁺ was ~60μmol (Fig. 2a,b), the additional O₂ being generated from cobalt oxide derived from both cobalt complexes.

**Photocatalytic reactions using DCPIP as electron mediator**

Reactions using DCPIP in solution resulted in no measurable O₂ generation, presumably due to the intense deep blue coloured DCPIP blocking most incoming light. Also sol gels prepared incorporating Ru(bpy)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 SiO₂-DCPIP-Ru(bpy)₂⁺ gels and then a further photocatalytic reaction undertaken using the recovered and washed combined SiO₂/Ru(bpy)₂⁺/DCPIP/Co²⁺/³⁺ gel composite. Fig. 3 shows evolution of O₂ 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 SiO₂ microporous gel, which would otherwise quench the light generated Ru(bpy)₂⁺ state, was required for its successful use in the photocatalytic reactions (see ESI† for experimental details).

After 30 min of reaction a maximum O₂ yield of ~54μmol was obtained. 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 SiO₂ gel with incorporated reagents was then recovered by filtration, washed and degassed and used in a further photocatalytic reaction. After 30 min a reduced O₂ yield of ~38μmol of O₂ was obtained. The reduction in activity of the silica gel supported mixture was 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 SiO₂-DCPIP-Ru(bpy)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 DCPIP and DCPIP⁺ which allowed the red/orange colour of this, the Ru(bpy)₂⁺ and the cobalt complex to become visible (Fig. 4).
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$^{3+}$, 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$^{2+}$ due to Co$_3$O$_4$ (Fig. S).20-21

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$_3$O$_4$ and contained ~50mg of [Ru(bpy)$_3$Cl]Cl$_2$, though not all of this would be accessible for reaction.

A simple further test using a solution of 20% hydrogen peroxide to confirm presence of cobalt ions was conducted.

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$_3$O$_4$ 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.$^5$

$$2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \Delta \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad \text{(to DCPIP mediator)}$$

The suggested processes involved in water oxidation with the combined silica support are shown in Scheme 1a,b.
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 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$_3$ gas by-product liberated.

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Notes and references