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Photocatalytic H₂ evolution from neutral water with a molecular cobalt catalyst on a dye-sensitised TiO₂ nanoparticle^{†‡}Fezile Lakadamyali[§] and Erwin Reisner^{*§}

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We report on a self-assembled system comprising of a molecular H₂ production cobalt catalyst attached on a ruthenium dye-sensitised TiO₂ nanoparticle. Visible light irradiation of the dispersed nanoparticles in the presence of the sacrificial electron donor triethanolamine produces H₂ photocatalytically in pH neutral water and at room temperature.

Sunlight has enormous potential as a sustainable energy source, and the photochemical conversion of solar into chemical energy is attracting interest to replace fossil fuels.¹ The high specific energy carrier H₂—an ancient biological fuel²—can be produced from light and water by using principles adopted from photobiological H₂ production processes.³ In an artificial photosynthetic system, a photon induces a charge-separated state, which drives a fuel-forming cathodic process. To complete the redox cycle, the necessary electrons must be provided from the electron donor side of the system; ideally extracted from water itself in a four-electron process to release O₂.

Semiconducting metal oxides, in particular those of TiO₂, are extensively studied as inexpensive and environmentally benign photocatalysts for water splitting.⁴ Pure TiO₂ requires UV band gap irradiation (3.2 eV) and shows fast rates of electron–hole recombination and a high overpotential for H₂ (and O₂) evolution. The resulting poor photocatalytic efficiency can be considerably enhanced by (i) dye-sensitisation of TiO₂ to allow for visible light absorption,⁵ and (ii) co-attachment of an efficient H₂ production catalyst such as metallic Pt,⁶ or enzymes known as hydrogenases.⁷ An important requirement for a H₂ evolution catalyst to function on TiO₂ is that it operates with a small intrinsic thermodynamic driving-force (ΔE); the difference between the conduction band (CB) potential of TiO₂ and the H⁺/H₂ reduction potential is approximately 100 to 200 mV under acidic or pH neutral conditions.⁴

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Despite their excellent activity on TiO₂, Pt and hydrogenases have only limited scope for applications on an industrial scale, because of the high cost of the precious metal and the fragility of the enzyme. We were interested in finding a low-cost catalyst for proton reduction on TiO₂ and to attach it to a ruthenium dye-sensitised TiO₂ nanoparticle (NP) for visible light driven H₂ production (Fig. 1). Cobalt complexes with diglyoxime ligands (cobaloximes) appeared to be promising candidates, as they are known to evolve H₂ at low overpotential.⁸ An active Co^I species is formed upon reduction that reacts with a proton to produce a postulated Co^{III}-hydride, which releases H₂ *via* a homo- or heterolytic pathway.⁹

A cobaloxime complex deposited on a glassy carbon electrode was previously shown to act as a cathode for proton reduction in aqueous solution at pH < 4.5, with an overpotential of only 100 mV.¹⁰ In particular, [Co^{III}Cl(dmgh)₂(pyridine)] (dmgh₂ = dimethylglyoxime) has emerged as a promising catalyst. It produces H₂ electrocatalytically with a small overpotential,¹¹ and photocatalytically in a homogeneous system when it is covalently linked to a ruthenium or porphyrin photosensitiser in the presence of Et₃N (electron donor) and an organic solvent.¹² Photocatalytic H₂ evolution from pure water was reported recently with [Co^{III}Cl(dmgh)₂(pyridine)] in a homogeneous, diffusion-limited, multi-component system in the presence of a sacrificial electron donor.¹³

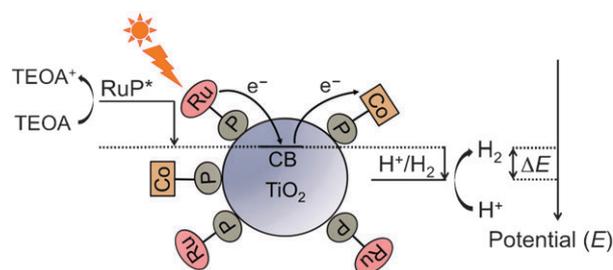


Fig. 1 Schematic representation of photocatalytic H₂ production TiO₂ NPs containing a covalently attached cobalt catalyst (CoP) and a ruthenium photosensitiser (RuP). The loaded NPs evolve H₂ in the presence of a sacrificial electron donor (triethanolamine, TEOA) at pH 7 and 25 °C. The available driving force (ΔE) for H₂ evolution is defined as the potential difference between the CB of TiO₂ and the H⁺/H₂ reduction potential. The chemical structures of CoP and RuP are depicted in Fig. 2.

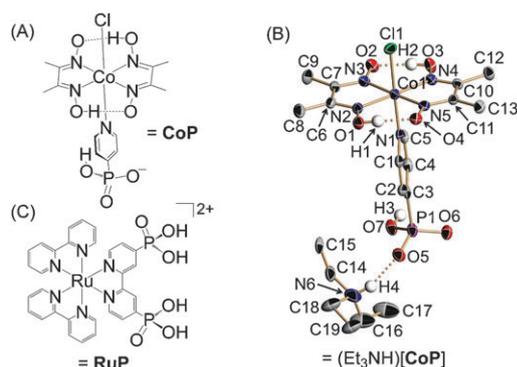


Fig. 2 Molecular structure of $(\text{Et}_3\text{NH})[\text{CoP}]$ as ChemDraw illustration (A) and based on X-ray coordinates showing 50% probability thermal ellipsoids and the atom-numbering scheme (B). The chemical structure of $[\text{RuP}]\text{Br}_2$ is also shown (C).

As a H_2 evolution catalyst for TiO_2 we synthesised $(\text{Et}_3\text{NH})[\text{Co}^{\text{III}}\text{Cl}(\text{dmgH})_2(\text{pyridyl-4-hydrophosphonate})]$, $(\text{Et}_3\text{NH})[\text{CoP}]$ (Fig. 2A), in one step from $[\text{CoCl}_2(\text{dmgH})(\text{dmgH}_2)]$ upon deprotonation of dmgH_2 and chloride displacement by pyridyl-4-phosphonic acid (54 mg, 67%).[¶] We introduced a phosphonate anchor group to the cobaloxime to provide a linkage to the metal oxide. The **CoP** anion crystallises with a counter-cation, Et_3NH^+ (Fig. 2B), with average imine $\text{Co}-\text{N}$ and the $\text{Co}-\text{Cl}$ bond distances of 1.90 and 2.22 Å; in agreement with the respective bond lengths of 1.90 and 2.23 Å in $[\text{CoCl}(\text{dmgH})(\text{dmgH}_2)(\text{methyl-4-pyridylcarboxylate})]$.¹⁴ **CoP** shows the expected distorted octahedral coordination geometry with a pyridine and a chlorido ligand in the axial location and a pair of dmgH^- ligands joined in the equatorial plane through intramolecular hydrogen bonds between the oxime oxygen atoms [$\text{O}1 \cdots \text{O}4$, 2.474(4) Å; $\text{O}3 \cdots \text{O}2$, 2.487(4) Å]. A hydrogen atom, H3, could be located on the difference Fourier map at the phosphonate group at **CoP**, and a proton, H4, at N6 of Et_3NH^+ . A H-bonding network is observed between the ammonium cation and the hydrophosphonate group [$\text{N}6 \cdots \text{O}5$, 2.734(5) Å] as well as the hydrophosphonate moieties of two neighboring **CoP** anions with $\text{O}6 \cdots \text{O}7'$ of 2.543(4) Å (see ESI[†]).

First, we investigated the binding of **CoP** to TiO_2 (Evonik Aeroxide P25, 21 nm diameter). A strong UV-vis absorption band at 245 nm of $(\text{Et}_3\text{NH})[\text{CoP}]$, assignable to a $\pi-\pi^*$ transition, allowed us to establish that one third of **CoP** (0.1 μmol) is indeed adsorbed on TiO_2 (5 mg) after stirring it for one hour in triethanolamine (TEOA) buffered aqueous solution (1.5 mL, 0.10 M, pH 7; see ESI[†]).

Then, a photocatalytic system containing **CoP**-modified TiO_2 NPs was assembled: $(\text{Et}_3\text{NH})[\text{CoP}]$ (0.1 μmol) was added to a stirred dispersion of TiO_2 NPs (5 mg) in TEOA buffer (4.5 mL, 0.10 M, pH 7) in a Pyrex vessel (headspace volume 4.85 mL). The dispersion was stirred at room temperature for one hour. All manipulations until this stage were made open to air, but the vessel was then tightly sealed with a rubber septum and purged with 2% CH_4 (internal GC standard) in N_2 .

UV light-driven H_2 production with stirred **CoP**-modified TiO_2 NPs is shown in Fig. 3. The headspace gas composition was regularly monitored by GC analysis, with the amount of evolved H_2 quantified against the internal CH_4 standard

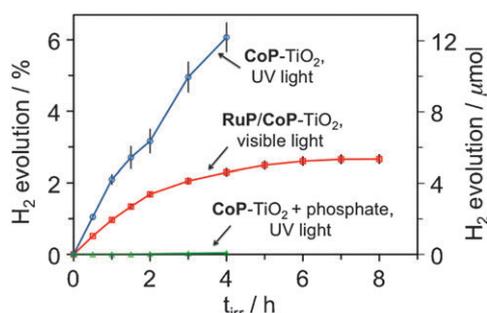


Fig. 3 Photocatalytic H_2 production with **CoP**-modified TiO_2 NPs in TEOA solution at pH 7 and 25 °C. UV irradiation results in H_2 production (blue trace), which is completely quenched in the presence of phosphate (25 mM, pH 7; green trace). Visible light driven H_2 evolution with **RuP/CoP**-modified TiO_2 is shown by the red trace, and standard deviations are given as vertical black lines.

(see ESI[†]). An accumulation of $6.07 \pm 0.42\%$ H_2 after four hours of irradiation and the formation of $4.2 \pm 0.3 \mu\text{mol H}_2 \text{ h}^{-1}$ with an initial turnover frequency (TOF) of $42 \pm 3 \text{ mol H}_2 \text{ h}^{-1} (\text{mol total CoP})^{-1}$ was observed in TEOA buffer at pH 7 and 25 °C. Thus, UV-light generated CB electrons of TiO_2 are transferred to **CoP** and the relatively small over-potential (ΔE) is sufficient to promote proton reduction.

Removal of free **CoP** in solution from this system by centrifugation and dispersion of the particles in fresh buffer resulted in the formation of $1.6 \pm 0.08\%$ H_2 after four hours of UV irradiation. The reduced activity is in agreement with the reduction of total **CoP** in the reaction mixture. When **CoP** is added to TiO_2 in TEOA buffer containing phosphate (25 mM) at pH 7, no H_2 was detected during UV irradiation as phosphate blocks the TiO_2 surface, leaving no space for **CoP** to adsorb (Fig. 3). No H_2 was produced (in the absence of phosphate) when we used only visible light (UV filter, $\lambda < 420 \text{ nm}$).

Finally, a photosensitiser was co-attached to TiO_2 for visible light absorption. We selected $[\text{Ru}^{\text{II}}(2,2' \text{-bipyridine})_2(2,2' \text{-bipyridine-4,4' \text{-diylbis(phosphonic acid)})\text{Br}_2$, **[RuP]Br₂** (Fig. 2C), which attaches tightly (>95%) to TiO_2 under pH neutral conditions.^{6a,7a} The photocatalytic system was assembled as described above, with the exception that **[RuP]Br₂** (0.1 μmol) was added to **CoP**-modified TiO_2 (see ESI[†]). TiO_2 serves as a readily dispersed semi-heterogeneous host for **RuP** and **CoP** with a loading ratio of approximately three to one, respectively (see ESI[†]). The stirred reaction vessel containing the dispersed **RuP/CoP**-modified TiO_2 NPs was exposed to visible light from a solar light simulator (100 mW cm^{-2}) equipped with a 420 nm UV filter. H_2 was produced at an initial rate of $1.94 \pm 0.1 \mu\text{mol H}_2 \text{ h}^{-1}$ and a TOF of $19 \pm 1 \text{ mol H}_2 \text{ h}^{-1} (\text{mol total CoP})^{-1}$ in TEOA buffer at pH 7 and 25 °C. The activity of the system started to decrease after approximately two hours and ceased after eight hours; resulting in a final turnover number of $53 \pm 4 \text{ mol H}_2 (\text{mol total CoP})^{-1}$ and an accumulation of $2.29 \pm 0.2\%$ H_2 in the headspace. The photostability during visible irradiation is presumably caused by **RuP**, because no significant decrease in activity was observed during UV irradiation in the absence of **RuP** (Fig. 3). Phosphonate-free $[\text{Co}^{\text{III}}\text{Cl}(\text{dmgH})_2(\text{pyridine})]$ adsorbed only marginally on TiO_2 ($\leq 5\%$), and a significantly reduced photoactivity ($0.28 \pm 0.1\%$ H_2 after four hours) was

observed when it was used instead of **CoP** during visible light irradiation.

When the pH of the system was altered from pH 7, H₂ production was significantly decreased: at pH 6, 0.06 ± 0.01% H₂ and at pH 8, 1.1 ± 0.06% H₂ were observed after four hours of visible light irradiation at 25 °C. Rates of catalysis scale with amount of light and catalysts. Irradiation of **RuP/CoP**-modified TiO₂ with reduced light intensity (20 mW cm⁻²) reduces the activity to 0.77 ± 0.04 μmol H₂ h⁻¹, and reduction of **RuP** to 0.02 μmol results in 1.07 ± 0.06 μmol H₂ h⁻¹ (with 100 mW cm⁻² irradiation). Reduction of **CoP** to 0.02 μmol yielded 0.20 ± 0.12 μmol H₂ h⁻¹. Separation of free **CoP** and **RuP** by centrifugation and dispersion of the modified TiO₂ particles in fresh buffer reduced the activity to 0.28 ± 0.08 μmol H₂ h⁻¹. In the absence of either light, **RuP**, TiO₂, **CoP**, or TEOA only tiny traces or no H₂ were detected under the same experimental conditions (see ESI†).

We propose that the dispersed **RuP/CoP**-modified TiO₂ NPs can operate by the following mechanism: **RuP** harvests visible light and the excited photosensitiser promotes electrons to the CB of TiO₂. The CB electrons are then transferred to **CoP**, which catalyses the evolution of H₂ ($E, H^+/H_2 = -0.42$ V vs. NHE, pH 7). The redox cycle is completed by oxidation of the sacrificial electron donor TEOA and recovery of oxidised **RuP** (Fig. 1). A requirement for this system to work is that the catalysts are, at least weakly, adsorbed to TiO₂.

Our system demonstrates that a first-row transition metal complex can serve as the H₂ evolution catalyst on TiO₂, giving an inexpensive alternative to Pt and a hydrogenase. A direct comparison with a related system containing a [NiFeSe]-hydrogenase from *Desulfomicrobium baculatum* on **RuP**-sensitised TiO₂ NPs is available (TEOA buffer, pH 7, 25 °C, visible light): on a “*per active*” site basis (at low enzyme loading on TiO₂), [NiFeSe]-hydrogenase evolves H₂ with a TOF of 50 (mol H₂) s⁻¹ (mol catalyst)⁻¹, and yields (at high enzyme loading) 2900 μmol H₂ h⁻¹ (g TiO₂)⁻¹.^{7a} Although the TOF of **CoP** is low (0.005 s⁻¹), it is remarkable that **RuP/CoP**-modified TiO₂ NPs produce about 400 μmol H₂ h⁻¹ (g TiO₂)⁻¹; a respectable “*per particle*” activity due to the small footprint of the synthetic catalyst.

In summary, a photoactive H₂ evolution system consisting of a cobaloxime on a dye-sensitised TiO₂ NP is reported. This system is facile to assemble, works under visible light irradiation in pH neutral water (free of organic solvents) and a small thermodynamic driving force is sufficient to drive proton reduction with **CoP**. TiO₂ NPs show excellent dispersibility in water and the high surface area allows for easy variation of the catalyst loading and ratio for the optimisation of light absorption and catalysis. Surface attachment of a small molecule catalyst may ultimately allow for the preparation of a low-cost H₂ evolving cathode for water electrolysis and utilisation in a photoelectrochemical water splitting cell. Further studies are underway in our laboratory to improve the stability of the cobalt catalyst on TiO₂ and to utilise this concept to drive other energetically uphill redox transformations with sunlight.

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Fellowship (EP/H00338X/1 to E.R.) and The University of Manchester. Dr Masaru Kato, Dr Nicoleta Muresan and Miss Ellen Swift are acknowledged for assistance in the synthetic part of the work and Dr Christopher Muryn for his help with crystallography. We are grateful to Evonik Industries for providing us with samples of TiO₂.

Notes and references

† Synthetic procedure and characterisation of (Et₃NH)[CoP]. Et₃N (21 μL, 0.15 mmol) was added to a stirred, green suspension of [CoCl₂(dmgH)(dmgH₂)] (54 mg, 0.15 mmol) in MeOH (4 mL), resulting in a brown solution. Pyridyl-4-phosphonic acid (24 mg, 0.15 mmol) was added after five minutes and the reaction mixture was heated at 40 °C for one hour. The solution was allowed to cool to room temperature and ethyl acetate (10 mL) was added slowly to precipitate the brown product, which was filtered off, washed with ethyl acetate and dried under high vacuum. Yield: 62 mg, 67%. Found: C, 38.6; H, 6.1; N, 14.1; Cl, 5.9; P, 5.1%. C₁₉H₃₅N₆ClCoO₇P requires C, 39.0; H, 6.0; N, 14.4; Cl, 6.1; P, 5.3%. δ_H (400 MHz, D₂O) 8.05 (2H, m, py), 7.53 (2H, m, py), 3.20 (6H, q, CH₃CH₂NH), 2.42 (12H, s, -CH₃), 1.28 ppm (9H, t, CH₃CH₂NH). Mp 198 °C (recrystallised from MeOH/EtOAc). ESI-MS, *m/z* (MeOH), +ve: found 102 (requires 102 for Et₃NH⁺), -ve: found 482 (requires 482 for [CoP]⁻). λ_{max}(H₂O)/nm 247 (ε/dm³ mmol⁻¹ cm⁻¹ 22), 225 (43). Single crystal X-ray analysis. (Et₃NH)[CoP]_{1/2}MeOH was crystallised from a MeOH solution with ethyl acetate vapor diffusion as brown blocks, mounted in Paratone N oil and transferred to the cold N₂ gas stream of the diffractometer. Crystal data: C_{19.5}H₃₇ClCoN₆O_{7.5}P, *M_r* = 600.90, triclinic, *a* = 8.171(5), *b* = 12.998(5), *c* = 14.602(5) Å, α = 113.768(5)°, β = 99.000(5)°, γ = 97.294(5)°, *V* = 1370.5(11) Å³, *T* = 100 K, space group *P*1̄, *Z* = 2, 8129 reflections measured, 4830 unique which were used in all calculations. The final *R*₁(*F*²) was 0.0499.

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