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Abstract

Photoelectrochemical cells that efficiently split water into oxygen and hydrogen, "the fuel of the future", need to combine robust water oxidation catalysts at the anode ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) with hydrogen reduction catalysts at the cathode ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). Both sets of catalysts will, ideally, operate at low overpotentials and employ light-driven or light-assisted processes. In this Perspective article, we focus on significant efforts to develop solid state materials and molecular coordination complexes as catalyst for water oxidation. We briefly review the field with emphasis on the various molecular catalysts that have been developed and then examine the activity of molecular catalysts in water oxidation following their attachment to conducting electrodes. For such molecular species to be useful in a solar water-splitting device it is preferable that they are securely and durably affixed to an electrode surface. We also consider recent developments aimed at combining the action of molecular catalysts with light absorption so that light driven water oxidation may be achieved.

Keywords

catalysts, water, photoelectrochemical, molecular, cells, oxidation

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Molecular water-oxidation catalysts for photoelectrochemical cells

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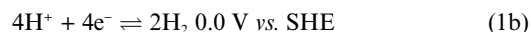
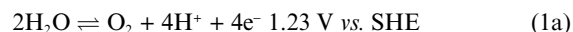
Photoelectrochemical cells that efficiently split water into oxygen and hydrogen, “the fuel of the future”, need to combine robust water oxidation catalysts at the anode ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) with hydrogen reduction catalysts at the cathode ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). Both sets of catalysts will, ideally, operate at low overpotentials and employ light-driven or light-assisted processes. In this *Perspective* article, we focus on significant efforts to develop solid state materials and molecular coordination complexes as catalyst for water oxidation. We briefly review the field with emphasis on the various molecular catalysts that have been developed and then examine the activity of molecular catalysts in water oxidation following their attachment to conducting electrodes. For such molecular species to be useful in a solar water-splitting device it is preferable that they are securely and durably affixed to an electrode surface. We also consider recent developments aimed at combining the action of molecular catalysts with light absorption so that light driven water oxidation may be achieved.

Introduction

The development of efficient technologies that produce carbon-free renewable fuel is vital if we are to meet the challenge of satisfying the energy needs of the future. Hydrogen gas is a high density, carbon-free energy carrier which is considered a potential “fuel of the future”. Hydrogen is readily produced on a large scale by steam reforming of natural gas or by partial oxidation and subsequent reforming of coal. Both of these processes produce significant carbon dioxide, are non-renewable and more expensive than conventional fuel sources.¹ Ideally, hydrogen should be

produced free of carbon, from the splitting of water using a renewable energy source, such as wind or solar energy.

The minimum theoretical electrical potential required to oxidize water (eqn (1a)) under standard conditions is 1.23 V (vs. standard hydrogen electrode (SHE), pH 0).²



In practice, however, an overpotential is needed that depends upon the ability of the catalyst to stabilize the highest energy intermediates. Overpotentials as low as 0.32 V have been achieved for the best noble metal catalysts.^{3,4} Additionally, other factors must be overcome in standard electrolyzers including: (i) cell resistance (proton and electron current resistances, electrolyte

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Robin Brimblecombe was awarded a PhD in 2009 from Monash University, Melbourne, Australia, for the development of bio-inspired molecular water-oxidation catalysts. Robin completed a Fulbright Fellowship in Professor Dismukes' laboratory at Princeton University, USA, during 2007–08. He is currently a post-doctoral fellow in the group of Professor Spiccia at Monash University, working on the development of photo-electrochemical devices for water splitting.



G. Charles Dismukes

Chuck Dismukes obtained his PhD in 1976 from the University of Madison at Wisconsin, USA, under Prof. John Willard. Following two years of postdoctoral studies in biological chemistry with Professors Kenneth Sauer and Melvin Klein at the University of California, Berkeley, CA, USA, in 1978 he joined the Princeton University Chemistry faculty as an Assistant Professor. Currently he is a professor of chemistry and affiliated faculty member in the Princeton Environmental Institute and Princeton Materials Institute.

conductivity, ionic gas permeability); and (ii) irreversible processes (extraneous charge polarization, generation of terminal intermediates). The actual voltage required to achieve water electrolysis is therefore typically 1.85–2.05 V.^{3,5} This correlates to an overpotential requirement of at least 0.5–0.7 V.

In principle, the abundant solar energy resource could be utilized to provide this electrical potential. One approach for achieving this goal is the use of commercially-available photovoltaic cells to power water electrolyzers. This process has been demonstrated to yield solar-to-hydrogen efficiencies of up to 7%.⁶ However, silicon solar cells generate a maximum voltage of only around 0.6 V, and typical electrolyzers operate at around 2 V. Four silicon cells must therefore be used in series to generate the required voltage to bring about hydrogen formation. The requirement for four silicon cells and the additional cost of an electrolyser, makes hydrogen production from water using this technology uneconomical for large scale applications, with an estimated cost of \$28 kg⁻¹ (1 kg of hydrogen is energetically roughly equivalent to one gallon of gasoline).⁷ Alternative technologies such as dye sensitised solar cells (DSSCs)^{6,8} can also be used to drive water oxidation, but, even in this case, three DSSCs are needed to achieve water electrolysis.⁶

The key to achieving efficient, electrochemically driven water splitting using solar energy is to drastically lower the overpotential required for water oxidation. This can be done using catalysts that: (i) lower the free energy of the highest energy intermediates formed during the oxidation half reaction; and (ii) increase the specificity of products generated. Two critical features needed for such a catalyst to facilitate water oxidation are: 1) binding of the water substrate to sites that favour two-electron oxidation reactions, thereby by-passing the energetically unfavourable one-electron oxidised (radical) intermediates; and 2) close proximity of these sites to allow for O–O collision and bond formation in the peroxo intermediate. The first feature involves efficient proton-coupled electron transfer reactions with bound water. This can prospectively be provided by transition metal compounds capable of coordinating water. The optimal catalyst should couple the energy-intensive O–H dissociation steps with the energy-releasing step of O–O bond formation by rearranging these five bonds in a coordinated sequence without releasing reactive intermediates.

Delivering the necessary energy input into these bonds while overcoming this mechanistic complexity makes water oxidation photocatalysis one of the “holy grails” of chemistry.^{8,9}

Water oxidation catalysts have been broadly developed in two areas: solid metal-oxide catalytic surfaces,^{6,10–19} and inorganic molecular catalysts.^{20,21} A major challenge to solar water oxidation is that the catalysts must, in addition to being stable and having high turnover frequencies, be inherent collectors of solar energy (integrated catalysis/photoconversion) or readily incorporated onto conductive electrodes made from abundant (non-precious) materials (for indirect photoconversion).^{8,22,23}

In this *Perspective*, we briefly review the state of research on solid-state and inorganic molecular water oxidation catalysts with some emphasis on “bioinspired” molecular catalysts. Focussing on the development of devices incorporating molecular catalysts, we then discuss methods for immobilizing catalysts on electrode surfaces and coupling them to light absorbing antennae, for the ultimate purpose of achieving light-driven hydrogen generation.

Solid state catalysts

An extensive range of solid state materials are under evaluation for water oxidation catalysis, including a large and diverse family of transition metal oxides, which can be used either as electrocatalysts, or in the case of semiconducting metal oxides, for integrated catalysis/photoconversion. The most efficient electrocatalysts typically employ precious metals, such as Pt, Ru and Ir. They are usually driven with an externally applied potential.⁶ Progress is being made on development of alloys with improved stability and turnover rates,¹² but the fundamental limitation of availability and cost constitute a major barrier to the large scale application of these systems.

A recent development is the use of catalytically active transition metal oxide phases. One interesting example is the AB₂O₄ spinel phase,²⁴ which has been known for many years to be catalytically active with particles on the micron size scale. Nanoscopic particles of Co₃O₄ spinel have been found to exhibit considerably high catalytic water oxidation rates (TOF = 1140 s⁻¹ per Co₃O₄).⁴ Other active solid phases have been prepared by electrodeposition.



Gerhard F. Swiegers

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Gerry Swiegers grew up in Port Elizabeth, South Africa, at which University he completed a BSc (Hons) in chemistry. After completing his PhD with Professor Ulli Mueller-Westerhoff at the University of Connecticut, he held academic positions at the Australian National University and the University of Wollongong, Australia. In 1998 he joined the Commonwealth Scientific and Industrial Research Organization (CSIRO) as a research scientist.



Leone Spiccia

He is currently Professor of Chemistry at Monash University in 1987, where he is currently Professor of Chemistry.

Leone Spiccia obtained his PhD degree in 1984 from the University of Western Australia, Perth, Western Australia, under Dr Jack Harrowfield and Professor Don Watts. Following post-doctoral fellowships with Professor Tom Swaddle (University of Calgary), Professor Werner Marty (University of Neuchâtel) and Professor Alan Sargeson (Australian National University), he took up an academic appointment in the Department of Chemistry

For example, an amorphous, non-conducting Co:P:O phase forms upon electrooxidation of Co^{2+} that is catalytic in water oxidation.¹⁶ Currents of 1 mA cm^{-2} have been generated by these films at an overpotential of 0.5 V. This promising material is chemically unstable towards dissolution and loss of Co(II) ions, but can be repaired by the applied electrical potential in the presence of HPO_4^{2-} . This establishes a dynamic equilibrium between soluble Co^{2+} and HPO_4^{2-} species and the insoluble, catalytically active Co^{3+} - HPO_4^{2-} phase.

Metal oxides containing various combinations of Ti, Nb, Ta, W, Ga, In, Ge, Sn and Sb have been developed in an effort to utilize light to achieve efficient electrocatalytic oxidation of water. Like TiO_2 , many of these materials, including NaTaO_3 and SrTiO_3 , have large band gaps and only absorb a small portion of the solar spectrum. Others, such as WO_3 and Fe_2O_3 , have unsuitable band edge positions, so that the potential energy generated on absorption of light does not complement that required for the oxidation of water and the subsequent reduction of protons. Another class of catalysts, including CdS and CdSe, have narrow band gaps with ideal band edge positions but are unstable under the oxidative potentials required to drive water oxidation.¹³ Achieving the optimum balance between energy absorption and catalytic potential has, consequently, proven difficult using a single material. Recent materials of interest include doped binary semiconductors possessing a UV-blue light response.^{12,13}

Another approach towards overcoming these challenges is to couple appropriate combinations of materials.^{6,8,14,15,25} For example, the unsuitable band edge position of WO_3 and Fe_2O_3 can be overcome by coupling them in tandem to a photovoltaic device (Fig. 1). The additional potential required to split water is then generated by the photovoltaic device.⁶ Hydrogen generation efficiencies of 3% have been achieved by combining water electrolyzers containing these materials with DSSCs.⁶

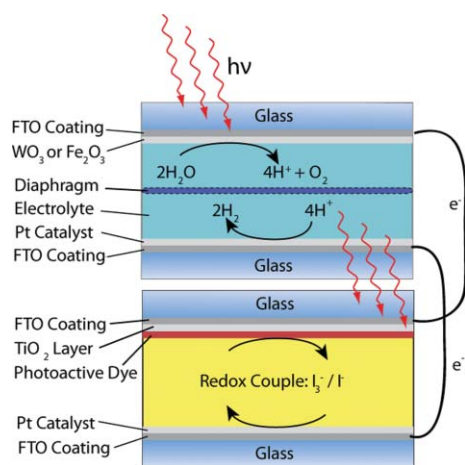


Fig. 1 Schematic representation of a tandem photoelectrochemical cell, combining a water photo-electrolyser with a dye sensitised solar cell.

This challenge is also being addressed by integrating multiple materials into a single electrode creating multi-junction devices, where the photoanode contains a layer of a water oxidation photocatalyst such as GaInP_2 , and a layer of photovoltaic material, such as a GaAs *p/n* junction; the latter provides the extra potential required to complete the circuit.²⁵

Other developments include depositing doped thin-film oxides (NiFeO_2 and Fe_2O_3) on multi-junction photocells. These catalysts exhibit longer stability and have been integrated with commercial multi-junction solar cells.^{14,15} However they typically still require large overpotentials and employ highly corrosive alkaline conditions ($\text{pH} = 14$).

In summary, solid film catalysts have the potential advantages of preparative simplicity and ready incorporation into devices.⁶ When prepared as high surface area nanostructured materials a large density of catalytic sites can be attained, leading to significant improvements in overall turnover number even for materials exhibiting modest specific activities per site.

Molecular catalysts

Molecular catalysts offer the prospect of specific tailoring of the atomic structure and composition without the constraints imposed by an extended solid lattice. Such catalysts could potentially lead to more efficient water oxidation as the O–H bond cleavage and O–O bond forming reactions can be simultaneously optimized. They may also be made from abundant (and cheap) materials.

The “bottom-up” design and development of a successful molecular catalyst is, however, an extremely challenging task. Thankfully, nature has spent the last 3 billion years optimizing a water oxidation system that is an excellent blueprint for the design of molecular water oxidation catalysts. This most efficient molecular water oxidation catalyst is the naturally-occurring *Water Oxidizing Complex* (also known as the Oxygen Evolving Centre) of *Photosystem II (PSII-WOC)*. *In vivo* activities of the *PSII-WOC* are known to reach turnover frequencies of *ca.* 1000 O_2 molecules s^{-1} site $^{-1}$, and turnover numbers of >1 million.²⁶ The active site of the *PSII-WOC* within oxygenic phototrophs comprises a CaMn_4O_x core,²⁷ whose structure and catalytic features are described in detail elsewhere.^{28–31} Beyond the cluster itself, the crucial step in successful water oxidation using solar energy by *PSII*, is the efficient removal of electrons from the cluster, *via* a conductive tyrosine residue (Y_2), coupled to the light adsorbing oxidative $\text{P680}^{0/+}$ complex.

Bio-inspired molecular catalysts

The water oxidation complex of *PSII* has inspired a wide range of model molecular water oxidation catalysts. The most successful of these utilize the transition metals Ru, Mn and Ir. As in the *PSII-WOC*, high oxidation states of these metals are generally stabilized by introducing electron donating ligands with oxygen and nitrogen donor atoms. A few examples of these molecular catalysts are described below as they have been reviewed in detail recently.²⁰

To date, Ru is the most widely used transition metal in water oxidation molecular catalysts. Ru complexes typically form stable metal–ligand bonds, which increase the stability of the reactive intermediates involved in water oxidation. As discussed below, however, strong ligand binding to terminal positions on the metal coordination sphere can also deactivate Ru-based catalysts by preventing further reaction.³² In addition, kinetically inert intermediates, typically Ru(II) species, may be involved in the catalytic cycle which would affect the catalyst turnover rates.

The first example of a homogeneous molecular water oxidation catalyst was the Ru^{III} dimer, [(bipy)₂(H₂O)Ru^{III}-ORu^{III}(H₂O)(bipy)₂]⁴⁺, where bipy = 2,2'-bipyridine (Fig. 2(a)). This complex has been shown to generate oxygen evolution at rates of 0.0042 molecules O₂ s⁻¹, for an average of 13 turnovers, using Ce(IV) as sacrificial oxidant.^{33,34} The mechanism by which this catalyst oxidizes water continues to be a subject of debate.^{32,35}

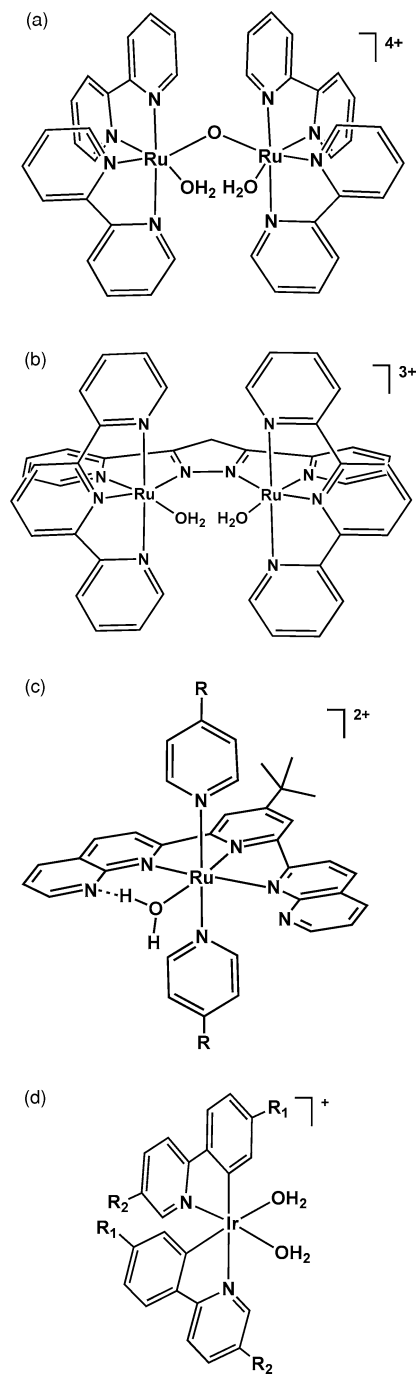


Fig. 2 Examples of ruthenium and iridium molecular catalysts: (a) [(bipy)₂(H₂O)Ru^{III}ORu^{III}(H₂O)(bipy)₂]⁴⁺; (b) [(terpy)₂(H₂O)Ru-(dpp)Ru(H₂O)(terpy)₂]³⁺; (c) [Ru(naphthyridyl)pyridyl-pyridazine](R-pyridine)₂²⁺; and (d) [Ir(R₁R₂phenylpyridine)₂(H₂O)₂]⁺.

Since its discovery, a range of oxo-bridged Ru dimer catalysts have been reported.³⁶ One subset of these catalysts are dinuclear Ru complexes bridged by amine-based ligands, such as [(terpy)₂(H₂O)Ru(dpp)Ru(H₂O)(terpy)₂]³⁺, where terpy = 1,2':6',2''-terpyridine and dpp = 2,4-(dipyridyl)pyrazole (Fig. 2(b)).³⁷ These complexes are reported to oxidize water both at a faster rate and with higher turnovers than the oxo bridged dimers.³⁷ They exhibit an oxygen evolution rate of 0.014 molecules O₂ s⁻¹ and a turnover number of 18.6, using Ce^{IV} as the oxidant. The increased rate and stability appears to be aided by the amine bridges which have been proposed to slow catalyst decomposition and promote water oxidation by placing the two ruthenium centres in close proximity. A dinuclear Ru complex supported by a (naphthyridyl)pyridyl-pyridazine ligand and four axially substituted pyridine ligands has been shown to be capable of water-oxidation catalysis at a rate of 7.7 × 10⁻⁴ molecules O₂ s⁻¹ for 3200 turnovers, using Ce^{IV} as an oxidant.³⁸

Very recently two mononuclear Ru complexes, [Ru(tpy)(bpm)-OH₂]²⁺ and [Ru(tpy)(bpz)OH₂]²⁺, where bpm = 2,2'-bipyrimidine and bpz = 2,2'-bipyrazine, have been reported to oxidise water.³⁹ Zong and Thummel have reported a series of mononuclear Ru(II) complexes that also oxidise water, with [Ru(pynap)(CH₃py)₂Cl]⁺, where pynap = 2-(pyrid-2'-yl)-1,8-naphthyridine (Fig. 2(c)), showing the fastest oxygen evolution rate and 580 turnovers.³⁸

A new class of molecular catalysts uses a single Ir^{III} centre supported by two phenyl pyridines and two water ligands, [Ir(R₁R₂phenylpyridine)₂(H₂O)₂]⁺ (Fig. 2(d)).⁴⁰ In homogeneous solution, using Ce⁴⁺ as a sacrificial oxidant, these complexes achieve maximum turnover frequencies of 1.5 × 10⁻³ molecules O₂ s⁻¹ and turnover numbers of 2500. By altering pendant functional groups of the phenyl pyridine ligands, the electrochemical properties of these complexes can be tuned; the authors suggest that this can facilitate efficient coupling to photosensitisers or electrode surfaces.⁴⁰

Several Mn molecular water oxidation catalysts have been inspired by the *PSII-WOC*. A diverse range of di- and tri-nuclear Mn complexes are described in the literature as “catalysts” for water oxidation. However, unequivocal evidence for oxygen evolution from water is available for few of these complexes and even fewer have proved capable of multiple turnovers.⁴¹ Among the most active complexes are those with [Mn₂O₂]ⁿ⁺ cores.^{23,42,43} The most notable examples are: [Mn₂^{II}(mcbpen)₂(H₂O)₂]²⁺ (mcbpen = *N*-methyl-*N'*-carboxymethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine, Fig. 3(b)),⁴³ [(tpy)(H₂O)Mn(μ-O)₂Mn(H₂O)(tpy)]³⁺ (tpy = 2,2':6',2''-terpyridine, Fig. 3(a)),^{13,44} and [Mn₂(OAc)₂(bpmp)]⁺ (bpmp = *N,N'*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine, Fig. 3(c)).⁴¹ These species display maximum catalytic rates in the range of 1.6–2.7 × 10⁻³ molecules O₂ s⁻¹ and modest turnover numbers (typically <20), when employing sacrificial chemical oxidants such as activated peroxides, hypochlorite, Pb^{IV} or Ce^{IV}.^{20,41,43,44} Few of these complexes are, in fact, able to directly oxidize water without *O*-transfer from the sacrificial oxidant. In homogeneous solution, the activity of [(tpy)(H₂O)Mn(μ-O)₂Mn(H₂O)(tpy)]³⁺ (Fig. 3(a))⁴⁴ depends on the presence of a 2e⁻ *O*-atom donor oxidant, such as HSO₅⁻ (oxone) or ClO⁻, to achieve four turnovers. Using one electron oxidants like Ce(IV), seventeen turnovers were observed when the complex was supported within the pores of a clay mineral.⁴⁵ In this case, the dependence of the rate of oxygen

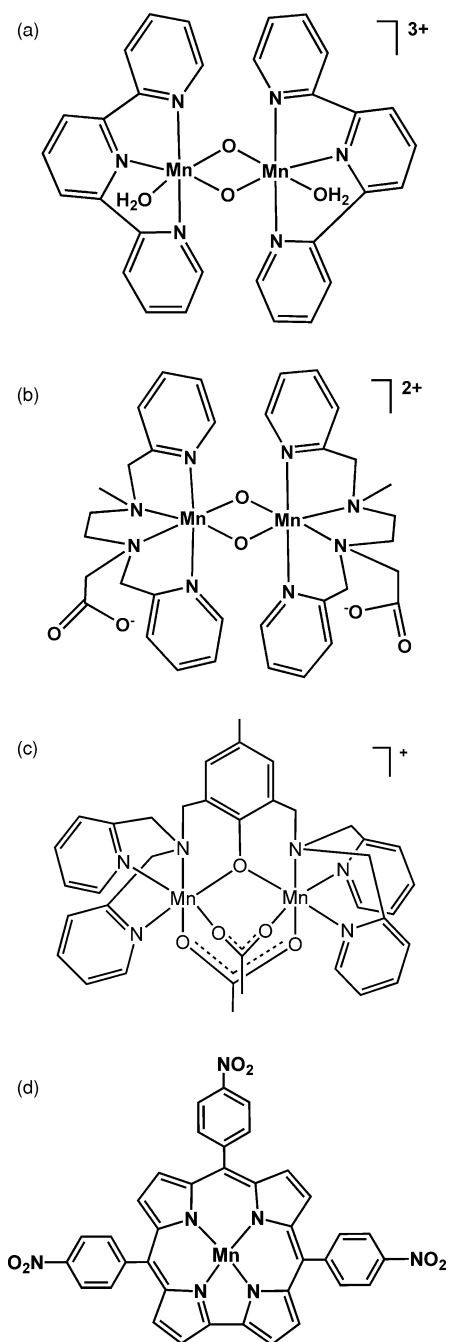


Fig. 3 Examples of manganese molecular catalysts that have achieved water oxidation using sacrificial chemical oxidants, such as OCl^- and HSO_5^- , $\text{Pb}(\text{OAc})_4$: (a) $(\text{tpy})(\text{H}_2\text{O})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{H}_2\text{O})(\text{tpy})^{3+}$; (b) $[\text{Mn}_2^{\text{II}}(\text{mcbpen})_2(\text{H}_2\text{O})_2]^{2+}$; (c) $[\text{Mn}_2(\text{OAc})_2(\text{bpmp})]^+$; and (d) $[\text{Mn}^{\text{III}}\text{-corrole}]^+$.

evolution on the square of the concentration of the catalyst within the clay layer suggested that water oxidation may involve dimer–dimer interactions. In addition, catalyst decomposition, involving dimer dissociation into monomers, was proposed to be slower within the clay layers. Styring, Kurz and co-workers have recently provided evidence for the direct oxidation of water by $[\text{Mn}_2(\text{OAc})_2(\text{bpmp})]^+$ when used in combination with either HSO_5^- or $\text{Pb}(\text{OAc})_4$.⁴¹ Gao *et al.*⁴⁶ very recently reported that

a $[\text{Mn}^{\text{III}}\text{-corrole}]^+$ complex can be converted into a $\text{Mn}^{\text{V}}\text{-oxo}$ complex which undergoes reductive elimination of oxygen on attack by hydroxide ion. An earlier study by Shimazaki *et al.*⁴⁷ found that a dimanganese(III)-porphyrin dimer is oxidised by *m*-chloroperbenzoic acid (*m*CPBA) to a dinuclear $\text{Mn}^{\text{V}}=\text{O}$ complex, which releases oxygen almost stoichiometrically on addition of acid. However, catalytic turnover was not demonstrated in these studies.

The molecular catalysts are generally used in conjunction with sacrificial oxidants. These oxidants are: (1) non-innocent in the reaction process; (2) consumed during the catalytic reaction; and (3) energetically inefficient in their operation (for example, Ce^{IV} has an oxidation potential of 1.72 V vs NHE). Although useful for probing the possible catalytic activity of molecular species and elucidating their reaction mechanisms in solution, use of such chemical oxidants in water-splitting photo-electrochemical devices is impractical.

Molecular catalysts for photoelectrochemical cells

To achieve sustained water oxidation in an electrochemical device, the molecular catalyst must be readily oxidized by the electrode surface. Only a few reports describe molecular catalysts that are oxidized by direct electron transfer at an electrode surface and then go on to catalyze water oxidation in homogeneous solution. Two such examples are: $[\text{WZnRu}_2(\text{OH})(\text{H}_2\text{O})(\text{ZnW}_9\text{O}_{34})_2]^{48}$ and $[(\text{bpy})_2(\text{H}_2\text{O})\text{RuORu}(\text{H}_2\text{O})(\text{bpy})_2]^{49}$. Catalysis in these systems is limited by diffusion of the catalyst to the electrode and the efficiency of the electron transfer between the catalysts and the electrode. To overcome these limitations, and optimize the catalytic effect, one therefore needs to immobilize the catalyst at the electrode surface.

Efficient coupling of the catalytic centre to an electron drain is also key to the success of the *PSII*–*WOC*. In this system, removal of electrons from the *WOC* as a result of water oxidation, occurs *via* a series of electron carriers. The electrons are eventually used, together with the protons formed during water oxidation, to convert carbon dioxide into carbohydrates. A water splitting photoelectrochemical cell aims to, similarly, oxidize water, generating oxygen, electrons and protons (Fig. 1, top device) which are then recombined at a counter electrode to form hydrogen gas. Bioinspired molecular catalysis for hydrogen production requires the catalysts to be electrically coupled to a conductive surface. Such coupling facilitates the efficient removal and collection of electrons during water oxidation. The device configuration needs to facilitate the separation of the gaseous products.

To date, remarkably few molecular catalysts have been immobilized and coupled to conductive surfaces for the purposes of water oxidation catalysis.

Immobilization of molecular catalysts by adsorption

One method of immobilizing molecular catalysts involves drop casting of water insoluble compounds onto electrode surfaces. A successful application of this method involved the deposition of layers of the active molecular catalyst $[\text{Ru}_2^{\text{II}}(\text{OH})_2(3,6\text{-}i\text{-Bu}_2\text{quinone})_2(\text{btpyan})]^{2+}$ (see Fig. 4(a); *btpyan* = 1,8-bis(2,2':6'2'')-terpyridylanthracene). When deposited onto an indium tin oxide (ITO) electrode, the catalyst layer was able to electrochemically

oxidize water to oxygen. A turnover number of 6730 was achieved under an applied potential of 1.7 V (vs. Ag/AgCl, pH 4.0[†]).⁵⁰ This is one of the highest turnover numbers reported for a molecular catalyst. After 40 hours of operation, however, the catalyst was found to have detached from the electrode.

This technique has also been applied using the Mn cubane complex; [Mn₄O₄((RPh)₂PO₂)₆] (R = OMe, see Fig. 4(b)). The cluster was either drop-cast or mechanically rubbed onto electrode surfaces and immersed in aqueous electrolyte (Fig. 5(a)). When polarized at 1.00 V (vs. Ag/AgCl, pH 7.0) and illuminated with light, a measurable photocurrent corresponding to water oxidation, was observed.⁵¹ However, as in the previous system, the solid films were found to detach from the electrode after several hours. This immobilisation method, consequently, appears to be unsuitable for the construction of a robust photoelectrochemical device.

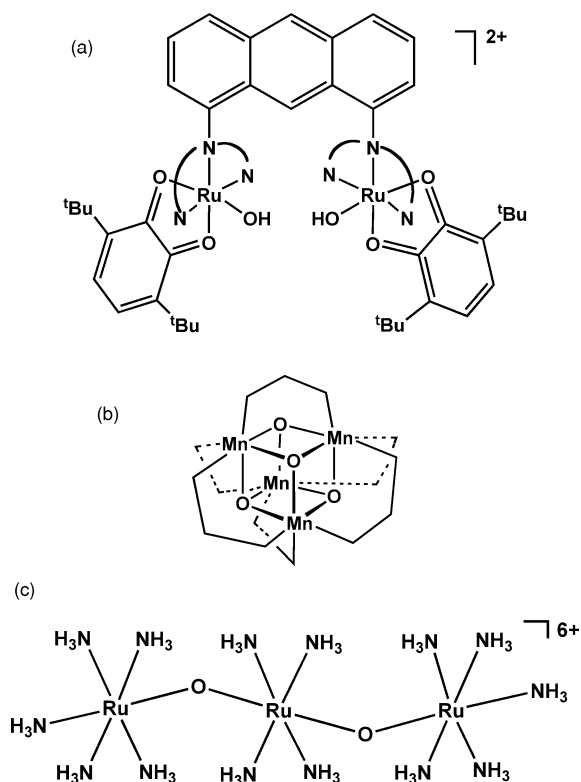


Fig. 4 Schematic representations of: (a) $[(\text{Bu}_2\text{qui})(\text{OH})\text{Ru}^{\text{II}}(\text{btpyan})\text{Ru}^{\text{II}}(\text{OH})(\text{Bu}_2\text{qui})]^{2+}$; (b) manganese cubane, $[\text{Mn}_4\text{O}_4((\text{RPh})_2\text{PO}_2)_6]$; (c) Ru-Red, $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\mu\text{-O})\text{Ru}^{\text{IV}}(\text{NH}_3)_4(\mu\text{-O})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{6+}$.

An alternative approach is to use Pt-black particles coated on a flat pyrolytic graphite electrode surface (Fig. 5(b)). For example, Ru-Red, $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\mu\text{-O})\text{Ru}^{\text{IV}}(\text{NH}_3)_4(\mu\text{-O})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{6+}$ (Fig. 4(c)), was drop cast over the coated electrodes (Fig. 5(b)) and when polarised at 1.3 V vs. Ag/AgCl quite rapid catalyst turnover ($0.30 \text{ molecules O}_2 \text{ s}^{-1}$) was observed.⁵² The impressive

[†] The Ag/AgCl electrode (in saturated KCl) is preferred as a reference to SHE for measurements conducted at variable pH. The potential of this couple is 0.20 V (vs SHE) and to convert a potential measured vs Ag/AgCl to the SHE scale simply add 0.20 V. Note, however, that SHE is measured at pH 0 and that the oxidation potential of water becomes 59 mV less positive with every increase in pH unit.

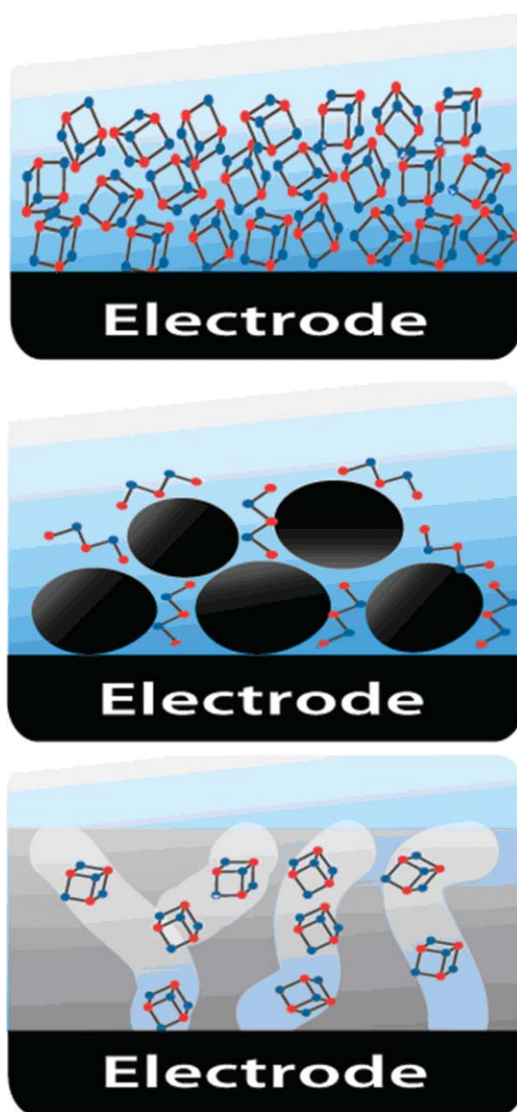


Fig. 5 Schematic representation of electrode immobilising techniques: (a) drop casting or mechanical rubbing of solid layer of catalyst on electrode surface; (b) drop casting of solid layer of catalysts onto Pt-particles coated on electrode surface; and (c) doping of catalyst into Nafion membrane coated on electrode surface.

performance of this system was attributed to efficient charge transfer from the Ru-Red to the electrode *via* the Pt-black particles.

An optimum ratio of Pt particles to Ru-Red was found, beyond which biomolecular decomposition caused a precipitous decline in activity.^{52,53} At the optimum ratio, this system is remarkably efficient per catalyst molecule. It is, however, limited in its practical utility for water oxidation devices because, at the high catalyst loadings required to achieve elevated current densities, the system is poorly active and has low stability. This same technique was successfully demonstrated for $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ /Pt-black particles and $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}(\mu\text{-O})\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ /Au particles as water oxidation catalysts.⁵³ Whilst the adsorption of solid layers of the molecular catalyst on electrode surfaces has been shown to be an effective means of investigating the electrocatalytic potential of some catalysts, the instability of the solid layer limits the

application of this method in the construction of electrochemical devices.

Polymer supported molecular catalysts

The use of a supporting matrix that holds the catalysts at the electrode surface and limits dissociation into the electrolyte is an alternative approach. The best studied examples are cation conducting membranes, such as Nafion (Fig. 5(c)).

Nafion is a fluorinated hydrophobic polymer with ionisable hydrophilic head groups (sulfonic acid). It can be cast on electrode surfaces to form membranes, within which the sulfonic acid or sulfonate groups (in the Na^+ form), generate hydrophilic channels roughly ~ 20 nm wide. These channels are permeable to protons and other cations but not anions.^{54,55} This property of Nafion has been exploited in a variety of applications, including as proton exchange membranes for various fuel cells, electrochromic devices and electrolyzers for H_2 generation.⁵⁶⁻⁵⁹

To immobilize a molecular catalyst, a solution of Nafion is typically deposited on a suitable electrode surface and allowed to dry. The resulting membrane is then doped with the desired catalyst, typically by cation exchange from solution. Doping can be confirmed using, for example, UV-visible spectrophotometry. The Nafion modified electrodes are then immersed in an appropriate electrolyte for electrochemical study. Due to the cation exchange properties of Nafion, this technique is best suited to catalysts that are cationic or to catalysts generated from cationic precursors.

The activity of several Nafion-supported Ru water oxidation catalysts, either when immobilised on electrode surfaces or when suspended in solution, has been examined.⁶⁰⁻⁶⁴ An early example involved the incorporation of Ru-red, $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\mu\text{-O})\text{Ru}^{\text{IV}}(\text{NH}_3)_4(\mu\text{-O})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{6+}$ (Fig. 4(c)), into an electrode coated with a Nafion membrane. The supported complex was demonstrated to be an active catalyst, with turnover rates of up to 3.1×10^{-3} molecules $\text{O}_2 \text{ s}^{-1}$. In the 1.4 V to 1.5 V potential region (*vs.* Ag/AgCl), over two thirds of the O_2 evolved from the electrode was found to arise from the action of the catalyst.⁶⁵

Turnover numbers were found to rise with increasing concentration of catalyst at low concentrations, reaching a maximum and then declining as the concentration was increased further. This trend was attributed to an initial increase in the number of catalytic sites and efficient charge transfer within the membrane at lower concentration. Bi-molecular decomposition was proposed to be responsible for the decrease in activity at higher concentrations.⁶⁵

Comparison of the water oxidation activity of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$, using Ce^{4+} as the sacrificial oxidant, both in solution and supported in Nafion, revealed that this catalyst exhibits higher activities when in a Nafion membrane than in homogeneous solution.⁶⁶ Slower catalyst decomposition within the Nafion channels was proposed to be responsible.

Nafion modified electrodes have also been used to immobilize a tetra-manganese cubane, $[\text{Mn}_4\text{O}_4\text{L}_6]^+$ where L = bis(*para*-methoxyphenyl)phosphinate or $(\text{MeOPh})_2\text{PO}_2$, for water oxidation catalysis. Electrodes bearing thin Nafion films (2–6 μm) were conveniently doped with the cationic cubane using an organic solution. Catalysis was achieved by polarizing the modified electrode at 1.0 V (*vs.* Ag/AgCl) under illumination with visible light. Light is needed as a driving force for this catalytic assembly to function in addition to the applied potential. It activates

the catalyst by inducing the release of one phosphinate ligand whereupon the cubane expels dioxygen. This is accompanied by the formation of reduced Mn compounds which, at the applied potential, are oxidised regenerating the catalytically active species. The action spectrum shows that the photocurrent generated tracks the electronic spectrum of the cubane, decreasing as the energy of incident light decreases.⁶⁷

Significantly larger photocurrents were observed for the cubane/Nafion system than for solid layers deposited as described above.⁵¹ For the Nafion system, peak turnover rates of 0.075 molecules $\text{O}_2 \text{ s}^{-1}$ and turnover numbers of > 1000 were observed over a period of operation of 65 hours.⁶⁸ Oxygen evolution was confirmed by mass spectrometry and the use of a non-aqueous, organic electrolyte yielded no photocurrent, confirming that water is needed to sustain the photocurrent. As the Mn cubanes are insoluble in aqueous solution, the Nafion membrane not only provided a means of electrically coupling the catalyst to the electrode surface, but also provided an interface for the catalyst to interact with water, without it leaching into the bulk solvent.

UV-visible spectrophotometric analysis revealed that only a small amount of Mn was present in the Nafion membrane, of which a fraction is electrochemically active.⁶⁸ Attempts to increase the photocurrent by increasing the concentration of cubane within the Nafion were unsuccessful.

The above studies demonstrated that Nafion membranes can provide an effective means of immobilizing molecular water oxidation catalysts on electrode surfaces. Nafion appears to provide greater stability of the catalytic layer than adsorbed solid layers. It may also play an important role in supporting water oxidation by providing pathways for the effective flow of electrons to the electrode surface and the migration of protons into the bulk aqueous solution. However, the current densities achieved thus far are too low to be practical in a photoelectrochemical device. This may be due to the limited number of catalyst host sites within the Nafion, with the remainder of the membrane made up of inert Teflon like polymer. Moreover, the inert Nafion-like polymer is non-conductive so that, only those species in contact with, or in close proximity to, the electrode surface will be active in catalysis.

A recent development utilizes the deposition of conducting polypyrrole polymers to immobilise a molecular water oxidation catalyst, $[\text{Ru}_2^{\text{II}}(\mu\text{-bpp})(\text{trpy})_2(\text{H}_2\text{O})_2]^{3+}$ where bpp = bis(2-pyridyl)pyrazolato and *t*-trpy = 4'-(*para*-pyrrolylmethylphenyl)-2,2':6',2'-terpyridine (Fig. 6), to electrode surfaces.⁶⁹ Anodic polymerisation of the complex yielded the corresponding polypyrrole derivative, firmly anchoring the complex to conductive surfaces, such as vitreous carbon sponges and fluoride-doped tin oxide (FTO), and establishing electrical contact between the catalyst

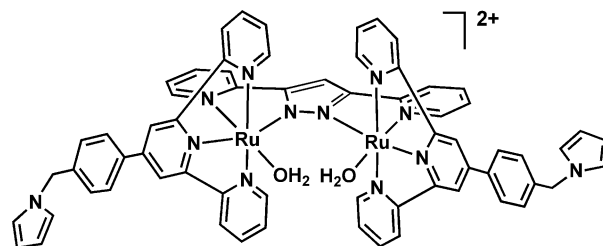


Fig. 6 $[\text{Ru}_2(\mu\text{-bpp})(\text{t-trpy})_2(\text{OH}_2)_2]^{2+}$ can be incorporated into a polypyrrole polymer on conductive electrode surfaces.

and electrode. Consequently, electrocatalytic water oxidation was achieved at an applied potential of 1.22 V (vs. Ag/AgCl) and turnover numbers of up to 120 were reported.⁶⁹

Chemically tethered molecular catalysts

In a dye sensitized solar cell (DSSC, Fig. 7), charge transfer to the electrode surface is achieved *via* a coordinate bond between the light absorbing dye (sensitizer) and a nanostructured semiconductor film (typically 5–20 μm thick) deposited on a conductive electrode surface.^{6,70} In the most commonly used Ru(II) bipyridyl or terpyridyl complexes,^{6,71,72,73} these ligands bear at least one carboxylate group, which strongly binds the TiO₂ surface. Dye attachment *via* carboxylate groups has also been applied to porphyrin and organic dyes. Other groups, such as phosphonates, have also been incorporated into the dyes as alternatives.^{74–76}

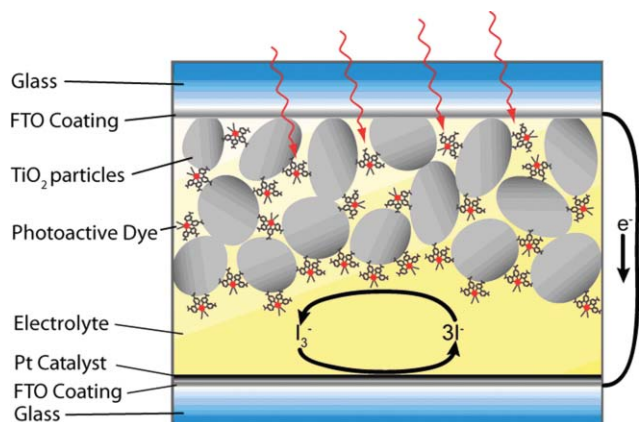


Fig. 7 Schematic representation of a dye sensitised solar cell.

The dye sensitized photoanodes, are then placed in contact with an electrolyte containing a redox couple, such as I⁻/I₃⁻, which is capable of regenerating the dye following excitation and charge separation and a Pt-coated cathode completes the cell. In these devices, the carboxylate groups not only immobilize the dye on the electrode, they also facilitate rapid electron transfer from the dye into the TiO₂. In DSSCs, this link is extremely stable and remains electrically active for millions of turnovers. Moreover, the fact that a direct bond is formed with the titania surface allows the creation of a monolayer of dye on the electrode surface which, when applied to nanostructured surfaces, facilitates the anchoring of many dye molecules over the thin nanostructured semiconductor layer. This leads to excellent light collection properties and large current densities.⁶

Two major challenges to using this method of surface attachment in photoelectrochemical water oxidation devices are, firstly, that the carboxylate–titania linkages are labile and undergo hydrolysis in aqueous environments resulting in detachment of the dye from the surface. Secondly, the Ru^{II}-polypyridyl complexes used in DSSCs are typically poor water oxidation catalysts.

The Mn-cubane molecules, described above, have been successfully attached to conducting electrodes through the formation of an indophenyl–gold bridge *via* one of the compounds' phosphinate ligands (Fig. 8(a)).⁷⁷ This was achieved by coating a gold surface with (4-indo-phenyl)phenyl phosphinic acid (IPPA) and then

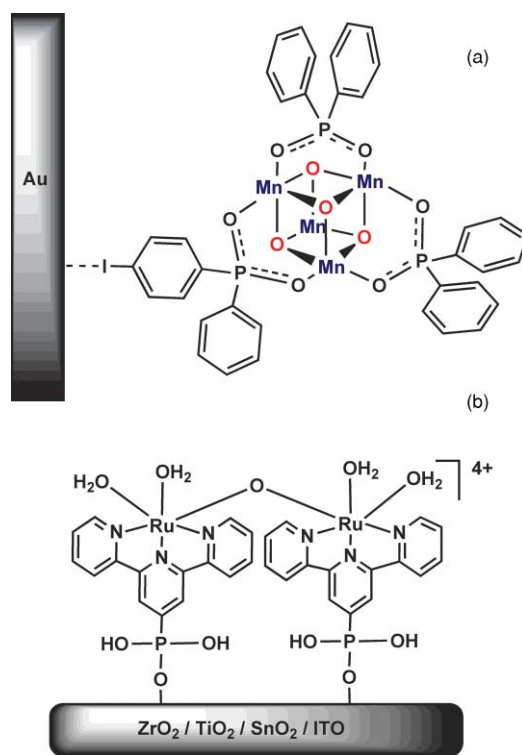


Fig. 8 Catalysts electronically and physically anchored to conducting electrode surfaces by covalent linkers: a) Manganese cubane anchored to a gold electrode *via* an indo-group on one of the di-phenyl phosphonate ligands; b) Ruthenium terpyridine dimer anchored to a range of oxide surfaces *via* phosphonate groups.

adsorbing Mn₄O₄(Ph₂PO₂)₆ from solution *via* a phosphinate ligand exchange reaction to yield Au-IPPA-Mn₄O₄(Ph₂PO₂)₅. The resulting monolayer was bound strongly to the gold surface and was not removed by sonication. Electrochemical measurements confirmed that the cubane had been successfully anchored on the Au-IPPA surface and that it was in electrical contact with the conductive gold surface. Unfortunately, the bridge was found to be oxidatively cleaved upon reaching the I⁻/IO₃⁻ potential, which is below the potential needed to generate the oxidised cubane state required for successful catalysis of water oxidation.^{68,77}

Successful covalent anchoring of an active molecular water oxidation catalyst was reported by Liu *et al.*⁷⁸ In this study, [(OH)₂OP(tpy)(H₂O)₂RuORu(OH)₂(tpy-PO(OH)₂)]⁴⁺ (tpy-PO(OH)₂ = 4'-phosphonic acid-2,2':6',2'-terpyridine) was tethered to a range of metal oxide electrode surfaces including ITO (Sn(IV)-doped In₂O₃), TiO₂, ZrO₂ and SnO₂ (Fig. 8(b)). Water oxidation was achieved by stepping the applied potential to either 1.15 V or 1.32 V at pH 6, with oxygen production confirmed using an oxygen-selective electrode. Maximum observed turnovers of 3 molecules O₂ per catalyst molecule were reported, with the catalytic current decaying to 10% of initial current after 1 hour of operation. The authors suggested that catalytic deactivation occurs *via* an oxidative cleavage mechanism analogous to that observed for similar complexes in homogenous solution. Although this system achieved limited catalytic turnover, it represents a significant advance in the successful covalent attachment of a functional molecular catalyst to an electrode surface.

Dye sensitization of molecular catalysts for photoelectrochemical cells

A critical aspect of light driven water oxidation is the sensitization of the molecular catalysts with light collecting antennae. On light absorption and charge separation, by electron injection into the electrode, such an antenna would be expected to generate an oxidation potential capable of extracting electrons from the water oxidation catalyst. The catalyst obtains these electrons by converting water into oxygen. This single-device approach contrasts with the tandem cell devices discussed earlier, which achieve water oxidation by coupling an electrode-bound catalyst to a photovoltaic cell *via* an external circuit. The PV cell generates the electrical bias required to drive the water oxidation process.⁶ As indicated earlier, four PV cells in series are needed since silicon PV generates a maximum voltage of 0.6 V. By using the catalytic systems described in the sections above, water oxidation could prospectively be achieved using as few as two PV cells in series. This is certainly possible for the DSSCs which can generate 0.75 V per device. It could be argued that water splitting devices of these types would be impractical and expensive. Commercial development of such tandem devices is, nevertheless, being pursued.⁷⁹

Coupling water oxidation catalysts directly to the light absorbing antennae within a single photoelectrochemical cell potentially offer significant advantages in terms of cost, but only when device efficiencies improve significantly. Several very recent reports of molecular catalysts sensitized by light absorbing complexes/materials have appeared.^{80,81} Non-molecular catalysts may also be sensitized by molecular light sensitizers.^{4,76}

Successful light-driven charge transfer between a Mn complex and TiO₂ particles has been achieved using an acetylacetonate anchor with a catechol-linker group (Fig. 9(a)). By utilizing this anchoring group, the researchers report rapid charge transfer upon light excitation.⁸⁰ Furthermore, the link was found to be stable in aqueous environments even under oxidative conditions. Unfortunately recombination of the excited electron with the Mn complex is very fast, resulting in a high probability of back

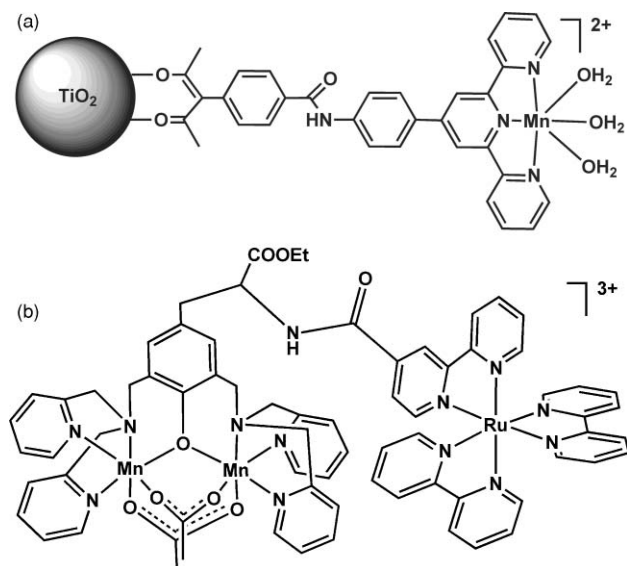


Fig. 9 Photosensitized manganese clusters: a) anchored to TiO₂; and b) electronically coupled to [Ru(bipyridine)₃]²⁺.

electron transfer after excitation, with an accompanying low injection efficiency. The authors used a mononuclear Mn complex, but to the present time no mononuclear Mn complexes have been shown to function as water oxidation catalysts. Despite the current limitations of the studied system, this approach offers the possibility of achieving high surface concentrations and efficient charge transfer for molecular catalysts.

A recent report of water splitting uses IrO₂ nanoparticles in combination with dye sensitized electrodes.⁷⁶ In this case, a light absorbing polypyridyl Ru complex was anchored to a TiO₂ electrode *via* phosphonate groups. These groups dissociate from the surface only slowly in an aqueous environment. Introduction of a catecholate group into the Ru complex allowed the attachment of IrO₂ nanoparticles, which are active in water oxidation catalysis (Fig. 10).⁷⁶

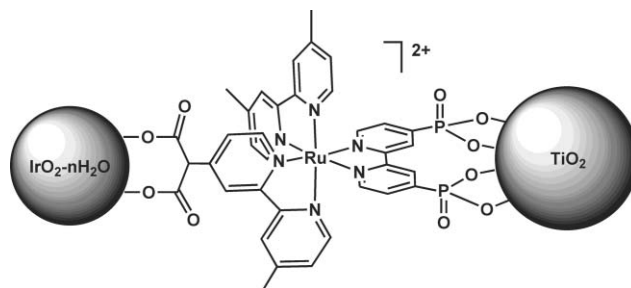


Fig. 10 Quasi-molecular water oxidation photoanode consisting of a film of TiO₂ nanoparticles on a conductive electrode (not shown), sensitized with a Ru^{II} tris(bipyridine) dye and IrO₂ catalytic nanoparticles.

As discussed above, the Ru dye absorbs light and transfers an electron into a bipyridyl π^* orbital (MLCT) from which it is injected into the conduction band of TiO₂. Mononuclear Ru^{II}-polypyridyl complexes are typically poor water oxidation catalysts, either being inactive or achieving turnovers too slowly to sustain a reasonable rate of light-driven water oxidation. In the work of Youngblood *et al.*, this limitation was overcome by adding a layer of catalytically active IrO₂ nanoparticles over the dye sensitized TiO₂ to aid water oxidation. The oxidised dye is capable of extracting electrons from the IrO₂ nanoparticles which, in turn, oxidise water (eqn 1(a)). With the assistance of a small applied potential, this system was found to be able to use light to oxidize water and generate hydrogen at the counter electrode (eqn 1(b)).⁷⁶

Although this system does not utilize a molecular water oxidation catalyst, it highlights the possibility of coupling a molecular catalyst to photosensitized titania in an aqueous environment.

The Styring and Hammarstrom groups have successfully demonstrated that high valence Mn complexes can be sensitized by Ru^{II} tris(bipyridyl) complexes using a chemical electron acceptor (Fig. 9(b)).⁸¹ We propose that the combination of these two approaches could prove effective. That is, the coupling of an efficient molecular water oxidation catalyst with an electrode bound light sensitizing complex would create a molecular mimic of not just the *WOC*, but the entire *PSII* charge separation process.

Conclusions

In this *Perspective* article, we have summarized a range of techniques for attaching molecular catalysts to either conductive

or semiconducting surfaces. The deposition of a solid layer of catalysts directly onto electrodes and the use of membranes to immobilize catalysts have proved most successful. The deposition of layers onto conductive electrodes has proven to be an effective means of studying the electrocatalytic potential of molecules. However, due to the instability of the solid layer this approach appears to have limited use in photo-electrochemical devices. The doping of the catalyst into polymer films offers greater stability than solid layers. Recent advances in controlling the concentration of catalysts at the electrode surface indicate that this technique could be successfully applied in the development of systems capable of generating high current densities. We note, however, that for the Ru complexes, competing bimolecular decomposition reactions at high catalyst loadings typically decrease the catalytic efficiency.^{52,53} In contrast, increasing the loading of Mn catalysts within a layered material enhances the rate of oxygen generation.⁴⁵ Thus, the incorporation of recently reported Mn catalysts⁴¹ into these polymer layers may lead to practical success at higher catalyst concentration. The potential of this approach has been demonstrated by our own recent work on a photocatalytic assembly that utilised a bio-inspired cubane cluster as water oxidation catalyst.^{51,68}

The covalent attachment of molecular catalysts to electrode surfaces represents another promising approach to developing an efficient solar water-splitting device. The most notable example in this respect, involved successful water oxidation by covalently linked Ru catalysts, with up to three oxygens evolved per catalyst.⁷⁸ In addition, successful photo-sensitization of several potentially catalytic clusters has been demonstrated.⁸¹ Thus, the individual processes required to achieve the efficient, sustained, light-driven molecular water oxidation in a photoelectrochemical cell have been demonstrated. Despite the progress described herein, however, efficient light-driven water oxidation by an *electrode bound molecular catalyst* remains unreported to date. Given recent progress on molecular catalysts and the report of a quasi molecular system, which coupled a Ru dye adsorbed on TiO₂ nanoparticles with an IrO₂ catalyst to achieve light driven water oxidation,⁷⁶ we anticipate that the combination of an electrode-bound water oxidation catalyst with a light sensitized electrode will be achieved in the near future.

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References

- M. L. Wald, in *Oil and the Future of Energy*, Scientific American, Guilford, USA, 2007.
- A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, Inc., New York, 1990.
- R. H. Jones, *Materials for the Hydrogen Economy*, Taylor & Francis Ltd, Hoboken, USA, 2007.
- F. Jiao and H. Frei, *Angew. Chem.*, 2009, **121**, 1873–1876.
- J. R. Wilson and G. Burgh, *Energizing Our Future: Rational Choices for the 21st Century*, John Wiley & Sons, Inc., Hoboken, USA, 2008.
- M. Grätzel, *Chem. Lett.*, 2005, **34**, 8–13.
- G. A. Olah, A. Goepfert, and G. K. Surya Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-vch, Los Angeles, 2006.
- M. Grätzel, *Nature*, 2001, **414**, 338–344.
- A. J. Bard, G. M. Whitesides, R. N. Zare and F. W. McLafferty, *Acc. Chem. Res.*, 1995, **28**, 91.
- T. Abe, K. Nagai, T. Ogiwara, S. Ogasawara, M. Kaneko, A. Tajiri and T. Norimatsu, *J. Electroanal. Chem.*, 2006, **587**, 127–132.
- N. P. Luneva, V. Y. Shafirovich and A. E. Shilov, *J. Mol. Catal.*, 1989, **52**, 49–62.
- K. Maeda, D. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295.
- K. Maeda, K. Teramura, D. S. Lu, N. Y. Inoue and K. Domen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7806–7809.
- E. L. Miller, R. E. Rocheleau and S. Khan, *Int. J. Hydrogen Energy*, 2004, **29**, 907–914.
- R. E. Rocheleau, E. L. Miller and A. Misra, *Energy Fuels*, 1998, **12**, 3–10.
- M. W. Kanan and D. G. Nocera, *Science*, 2008, **321**, 1072–1076.
- K. Maeda and K. Domen, *J. Phys. Chem. C*, 2007, **111**, 7851–7861.
- F. E. Osterloh, *Chem. Mater.*, 2008, **20**, 35–54.
- R. van de Krol, Y. Liang and J. Schoonman, *J. Mater. Chem.*, 2008, **18**, 2311–2320.
- C. W. Cady, R. H. Crabtree and G. W. Brudvig, *Coord. Chem. Rev.*, 2008, **252**, 444–455.
- M. Yagi, A. Syouji, S. Yamada, M. Komi, H. Yamazaki and S. Tajima, *Photochem. Photobiol. Sci.*, 2009, **8**, 139–147.
- P. J. Sebastian, *Int. J. Hydrogen Energy*, 2001, **26**, 115–115.
- M. Yagi and K. Narita, *J. Am. Chem. Soc.*, 2004, **126**, 8084–8085.
- A. Walsh, S.-H. Wei, Y. Yan, M. M. Al-Jassim, J. A. Turner, M. Woodhouse and B. A. Parkinson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 165119–165128.
- O. Khaselev and J. Turner, *Science*, 1998, **280**, 425–427.
- G. M. Ananyev and G. C. Dismukes, *Photosynth. Res.*, 2005, **84**, 355–365.
- G. C. Dismukes, *Science*, 2001, **292**, 447–448.
- B. Loll, J. Kern, W. Saenger, A. Zouni and J. Biesiadka, *Nature*, 2005, **438**, 1040–1044.
- J. Murray and J. Barber, *J. Struct. Biol.*, 2007, **159**, 228–237.
- W. Hillier and T. Wydrzynski, *Coord. Chem. Rev.*, 2008, **252**, 306–317.
- F. Rappaport and B. A. Diner, *Coord. Chem. Rev.*, 2008, **252**, 259–272.
- R. A. Binstead, C. W. Chronister, J. Ni, C. M. Hartshorn and T. J. Meyer, *J. Am. Chem. Soc.*, 2000, **122**, 8464–8473.
- S. W. Gersten, G. J. Samuels and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4029.
- J. A. Gilbert, D. S. Eggleston, J. Wyatt, R. Murphy, D.A. Geselowitz, S. W. Gersten, D. J. Hodgson and T. J. Meyer, *J. Am. Chem. Soc.*, 1985, **107**, 3855–3864.
- H. Yamada, W. F. Siems, T. Koike and J. K. Hurst, *J. Am. Chem. Soc.*, 2004, **126**, 9786–9795.
- E. L. Lebeau, S. A. Adeyemi and T. J. Meyer, *Inorg. Chem.*, 1998, **37**, 6476–6484.
- C. Sens, I. Romero, M. Rodriguez, A. Llobet, T. Parela and J. Benet-Buchholz, *J. Am. Chem. Soc.*, 2004, **126**, 7798–7799.
- R. Zong and R. P. Thummel, *J. Am. Chem. Soc.*, 2005, **127**, 12802–12803.
- J. J. Concepcion, J. W. Jurss, J. L. Templeton and T. J. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 16462–16463.
- N. D. McDaniel, F. J. Coughlin, L. L. Tinker and S. Bernhard, *J. Am. Chem. Soc.*, 2008, **130**, 210–217.
- K. Beckmann, H. Uchtenhagen, G. Berggren, M. F. Anderlund, A. Thapper, J. Messinger, S. Styring and P. Kurz, *Energy Environ. Sci.*, 2008, **1**, 668–676.
- J. Limburg, J. S. Vrettos, H. Y. Chen, J. C. de Paula, R. H. Crabtree and G. W. Brudvig, *J. Am. Chem. Soc.*, 2001, **123**, 423–430.
- A. K. Poulsen, A. Rompel and C. J. McKenzie, *Angew. Chem., Int. Ed.*, 2005, **44**, 6916–6920.
- J. Limburg, J. S. Vrettos, L. M. Liable-Sands, A. L. Rheingold, R. H. Crabtree and G. W. Brudvig, *Science*, 1999, **283**, 1524–1527.
- K. Narita, T. Kuwabara, K. Sone, K. I. Shimizu and M. Yagi, *J. Phys. Chem. B*, 2006, **110**, 23107–23114.
- Y. Gao, T. Åkermark, J. Liu, L. Sun and B. Åkermark, *J. Am. Chem. Soc.*, 2009, **131**, 8726–8727.

- 47 Y. Shimazaki, T. Nagano, H. Takesue, B.-Y. Ye, F. Tani and Y. Naruta, *Angew. Chem., Int. Ed.*, 2004, **43**, 98–100.
- 48 A. R. Howells, A. Sankarraj and C. Shannon, *J. Am. Chem. Soc.*, 2004, **126**, 12258–12259.
- 49 H. H. Petach and C. M. Elliott, *J. Electrochem. Soc.*, 1992, **139**, 2217–2221.
- 50 T. Wada and K. Tanaka, *Eur. J. Inorg. Chem.*, 2005, 3832–3839.
- 51 R. Brimblecombe, A. M. Bond, G. C. Dismukes, G. F. Swiegers and L. Spiccia, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6441–6449.
- 52 I. Ogino, K. Nagoshi, M. Yagi and M. Kaneko, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3431–3434.
- 53 M. Yagi and M. Kaneko, *Chem. Rev.*, 2001, **101**, 21–36.
- 54 A. Rollet, O. Diat and G. Gebel, *J. Phys. Chem. B*, 2002, **106**, 3033–3036.
- 55 N. P. Blake, M. K. Petersen, G. A. Voth and H. Metiu, *J. Phys. Chem. B*, 2005, **109**, 24244.
- 56 R. J. Mortimer and J. L. Dillingham, *J. Electrochem. Soc.*, 1997, **144**, 1549–1553.
- 57 J. Zhu, R. Sattler, A. Garsuch, O. Yopez and P. Pickup, *Electrochim. Acta*, 2006, **51**, 4052–4060.
- 58 Y. Park and Y. Yamazaki, *Solid State Ionics*, 2005, **176**, 1079–1089.
- 59 H. Park and W. Choi, *Langmuir*, 2006, **22**, 2906–2911.
- 60 H. Hagiwara, N. Ono, T. Inoue, H. Matsumoto and T. Ishihara, *Angew. Chem., Int. Ed.*, 2006, **45**, 1420–1422.
- 61 M. A. Gondal, A. Hameed and Z. H. Yamani, *Energy Sources*, 2005, **27**, 1151–1165.
- 62 R. Bandyopadhyay, S. K. Maiti and R. Bhattacharyya, *Inorg. Chem. Commun.*, 2002, **5**, 452–452.
- 63 K. Sayama, K. Yase, H. Arakawa, K. Asakura, A. Tanaka, K. Domen and T. Onishi, *J. Photochem. Photobiol., A*, 1998, **114**, 125–135.
- 64 K. Hashimoto, H. Irie and A. Fujishima, *Jpn. J. Appl. Phys.*, 2005, **44**, 8269–8285.
- 65 M. Yagi, K. Kinoshita and M. Kaneko, *J. Phys. Chem.*, 1996, **100**, 11098–11100.
- 66 M. Yagi and M. K. Kentaro Nagoshi, *J. Phys. Chem. B*, 1997, **101**, 5143–5146.
- 67 R. Brimblecombe, D. R. J. Kolling, A. M. Bond, G. C. Dismukes, G. F. Swiegers and L. Spiccia, *Inorg. Chem.*, 2009, **48**, 7269–7279.
- 68 R. Brimblecombe, G. F. Swiegers, G. C. Dismukes and L. Spiccia, *Angew. Chem.*, 2008, **120**, 7445–7448.
- 69 J. Mola, E. Mas-Marza, X. Sala, I. Romero, M. Rodriguez, C. Vinas, T. Parella and A. Llobet, *Angew. Chem., Int. Ed.*, 2008, **47**, 5830–5832.
- 70 M. Grätzel, *J. Photochem. Photobiol., C*, 2003, **4**, 145–153.
- 71 P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613–1624.
- 72 T. Bessho, E. Yoneda, J.-H. Yum, M. Guglielmi, I. Tavernelli, H. Imai, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2009, **131**, 5930–5934.
- 73 F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Graetzel, *J. Am. Chem. Soc.*, 2008, **130**, 10720–10728.
- 74 P. Pèchy, F. P. Rotzinger, M. K. Nazeeruddin, O. Kohle, S. M. Zakeeruddin, R. Humphry-Baker and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 1995, 65–66.
- 75 H. Zabri, I. Gillaizeau, C. A. Bignozzi, S. Caramori, M.-F. Charlot, J. Cano-Boquera and F. Odobel, *Inorg. Chem.*, 2003, **42**, 6655–6666.
- 76 W. J. Youngblood, S. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust and T. E. Mallouk, *J. Am. Chem. Soc.*, 2009, **131**, 926–927.
- 77 Y. Yu, M. Dubey, S. L. Bernasek and G. C. Dismukes, *Langmuir*, 2007, **23**, 8257–8263.
- 78 F. Liu, T. Cardolaccia, B. J. Hornstein, J. R. Schoonover and T. J. Meyer, *J. Am. Chem. Soc.*, 2007, **129**, 2446–2447.
- 79 Hydrogen-Solar, *The Tandem Cell - Basics*, <http://www.hydrogensolar.com/>, Accessed 27th of April, 2009.
- 80 S. G. Abuabara, C. W. Cady, J. B. Baxter, C. A. Schmittenmaer, R. H. Crabtree, G. W. Brudvig and V. S. Batista, *J. Phys. Chem. C*, 2007, **111**, 11982–11990.
- 81 P. Huang, A. Magnuson, R. Lomoth, M. Abrahamsson, M. Tamm, L. Sun, B. van Rotterdam, J. Park, L. Hammarström, B. Åkermark and S. Styring, *J. Inorg. Biochem.*, 2002, **91**, 159–172.