J|A|C|S
COMMUNICATIONS

Solar Driven Water Oxidation by a Bioinspired Manganese Molecular Catalyst

Robin Brimblecombe,[†] Annette Koo,[†] G. Charles Dismukes,[‡] Gerhard F. Swiegers,[§] and Leone Spiccia*,[†]

School of Chemistry, Monash University, Wellington Road, Clayton, Victoria 3800, Australia, Department of Chemistry & Chemical Biology, Waksman Institute, Rutgers University, Piscataway, New Jersey 08854, and Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia

Received November 27, 2009; E-mail: leone.spiccia@sci.monash.edu.au

Hydrogen (H_2) produced by using sunlight to split water into its elements ($2H_2O \xrightarrow{(h\nu)} O_2 + 2H_2$) has long been recognized as the ideal source of abundant, renewable, and clean fuel.[1] Solar hydrogen production from water has, however, been hampered by a lack of efficient catalysts, made from earth-abundant elements, which can be integrated into light-harvesting photochemical devices.[2] Herein, we describe a free-standing photoelectrochemical cell (PEC) which combines a photosensitizer with a *molecular* manganese complex to achieve water oxidation catalysis without application of an external bias.

A PEC converts light energy into chemical energy via two electrochemical half-reactions that are coupled through an electrolyte containing the reactants. In PECs, at least one of the half-reactions is driven by light. In the classical example, TiO_2 is used as a photocatalyst to oxidize water, producing O_2 gas, protons, and electrons.[3] The protons and electrons are combined at the cathode to form H_2 gas.[4] Unfortunately, TiO_2 has a large band gap (3−3.2 eV) and is only active in the UV region of the solar spectrum,[4,5] a shortcoming of many photocatalysts. Water oxidation photocatalysts have been researched to address this challenge using a range of metal oxides,[6−12] composite semiconductors,[5,13] metal oxynitrides and oxysulfides,[9] and molecular catalysts.[14,15] Progress to date on *molecular* water catalysts has demonstrated that catalytic turnover can be achieved using sacrificial chemical oxidants[14−16] or a potential bias,[14−16] but rarely light energy.

We recently reported the photon-assisted electro-oxidation of water using a catalyst inspired by the Mn_4Ca active site of the photosynthetic water oxidation complex (PSII-WOC),[17] a tetranuclear Mn-oxo cluster ($[Mn_4O_4L_6]^+$, **1**$^+$ or *"cubium"*, L = $(MeOPh)_2PO_2^-$).[18] When suspended within a Nafion membrane, coated on a conductive electrode and illuminated with visible light after biasing at a potential of 1.2 V (vs SHE) in aqueous electrolyte, the cluster generates a sustained photocurrent, oxygen gas, and protons. Using visible light, this reaction persists for >1000 catalytic turnovers. Light is required to induce the release of O_2 from the cubium (**1**$^+$) forming a reduced intermediate, which binds water and is oxidized by an external bias to regenerate the catalytically active species, thereby completing the catalytic cycle.[8,19] The catalytic properties of the PSII-WOC that are included in the design of the **1**$^+$/Nafion photoanode have been described.[20]

In the present study, the **1**$^+$/Nafion water oxidation catalyst has been combined with a TiO_2-supported Ru^{II} sensitizer, $[Ru^{II}(bipy)_2(bipy(COO)_2)]$ (**2**) (Figure 1). Ru^{II}-polypyridyl complexes carry out efficient charge separation in dye-sensitized solar cells (DSSC),[21,22] and as such, the present device is proposed to operate as shown in Figure 1B. On light excitation, the Ru^{II} dye injects an electron into the TiO_2 conduction band from where it flows into an external circuit. This generates $[Ru^{III}(bipy)_2(bipy(COO)_2)]^+$, a potent oxidant ($E_P^{red}$ = +1.4 V vs SHE)[23] capable of one-electron oxidations, including the cubane **1**→**1**$^+$, if suitably coupled. By interfacing these components into a multilayer device a *molecular* based PEC has been constructed which, like PSII, oxidizes water using only visible light.

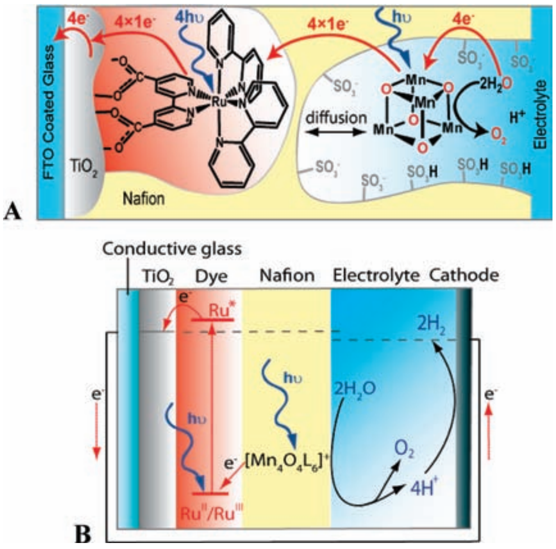

Figure 1. (A) Depiction of the photoanode consisting of a titania layer sensitized with the dye, $[Ru(bipy)_2(bipy(COO)_2)]$ (**2**), and coated with a Nafion film doped with $[Mn_4O_4((MeOPh)_2PO_2)_6]^+$ (**1**$^+$), showing the proposed operation of the device. (B) Cross-sectional arrangement of the PEC consisting of the photoanode **1**$^+$-Nafion/**2**-TiO_2, coupled to a Pt cathode via an aqueous electrolyte and an external circuit, showing the relative energy levels and proposed electron transfers.

This work complements a recent study by Mallouk and coworkers[13] which demonstrated that oxidation of water could be achieved on application of a modest external bias to a device coupling dye-sensitized TiO_2 to IrO_2 nanoparticles. Herein, we advance this concept by coupling an earth-abundant manganese catalyst (**1**$^+$) imbedded in a proton-conducting phase (Nafion) to a dye-sensitized titania photoanode. This system is capable of water oxidation *using only visible light and no external bias.*[24]

When supported in a Nafion membrane, the **1**$^+$ ↔ **1** electrolysis process generates a peak current at E_P^{red} = +1.12 vs SHE (Figure S1A), while the yield of **1**$^+$ and the electrocatalytic current both saturate at 1.2 V.[18] The reduction potentials of $[Ru(bipy)_3]^{3+}$ and $[Ru(bipy)_2(bipy(COO)_2)]^+$ (**2**), measured when suspended in a Nafion membrane supported on a glassy carbon electrode and immersed in aqueous electrolyte, are 0.2−0.3 V more positive than

---

[†] Monash University.
[‡] Rutgers University.
[§] University of Wollongong.

the potential needed to generate **1**$^+$ (Figure S1A), and in agreement with the potentials measured in organic solution.[23] Thus, in their Ru^{III} state, either dye is thermodynamically capable of oxidizing the reduced cubane species to the cubium. However, co-doping the dye and **1**$^+$ catalyst into the same Nafion film over a glassy carbon electrode did not generate any photocurrent in the absence of an applied potential (Figure S1).

Recognizing that charge separation from photoexcited Ru^{II*} complexes is very efficient in TiO_2 due to rapid electron injection, we explored whether a photocurrent could be generated by coupling of a dye-sensitized titania layer to a cubium-doped Nafion film. Protocols for assembling the device are described in the Supporting Information. Briefly, the dye, **2**, was absorbed onto TiO_2 films (400 nm particles) deposited on conductive glass (FTO). These dye-sensitized TiO_2 electrodes were then coated with Nafion and doped with **1**$^+$, as described,[18] to form the photoanode assembly, denoted as **1**$^+$-Nafion/**2**-TiO_2 (Figure 1B). Testing of the devices was carried out at pH 6.5 in an aqueous electrolyte containing 0.1 M Na_2SO_4.

The TiO_2 films alone generate little photocurrent (<1 μA) on illumination with light $\lambda > 290$ nm (black trace, Figure 2A) and are, therefore, incapable of catalysis of light-driven water oxidation under the conditions used. Sensitizing the TiO_2 film with the dye and coating with Nafion (denoted as Nafion/**2**-TiO_2) yields a transient current upon illumination (red trace, Figure 2A). The spike in photocurrent arises as the dye injects electrons into the TiO_2 layer and is oxidized to the Ru^{III} state. The inability of the oxidized dye to extract electrons from water (oxidize) and regenerate the Ru^{II} state leads to a sharp decline in photocurrent. Subsequent blocking of illumination generates a small current of opposite sign, as expected for the reversal of charge separation in a purely photovoltaic device.

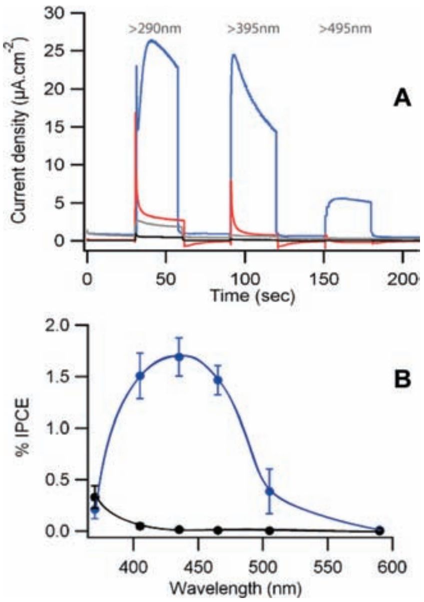

Figure 2. (A) Representative data from two electrode electrolysis experiments obtained at 22 °C for TiO_2 (4 mm × 4 mm) on conductive FTO coated glass (black), **1**$^+$- Nafion/TiO_2 (gray), Nafion/**2**-TiO_2 (red), and **1**$^+$-Nafion/**2**-TiO_2 (blue), illuminated at 100 mW/cm^2 through a series of long pass light filters, as labeled. (B) Average Incident Photon to Current Efficiency (IPCE) plot for **1**$^+$-Nafion/**2**-TiO_2 (blue) and TiO_2 (black) electrodes, with error bars displaying $\pm 1\sigma$ standard deviation.

Coating of TiO_2 with a **1**$^+$-Nafion layer in the absence of dye (denoted as **1**$^+$-Nafion/TiO_2) generates low photocurrents (gray trace, Figure 2A), similar to the untreated and dye-coated TiO_2 (postcurrent spike). However, when a layer of **1**$^+$-Nafion is applied over the dye-sensitized TiO_2 film, a large and sustained photocurrent is observed (blue trace, Figure 2A). No significant photocurrent was observed for **1**$^+$-Nafion/**2**-TiO_2 electrodes when the aqueous electrolyte was replaced with acetonitrile (0.1 M $BuNPF_6$), thus confirming the need for water.

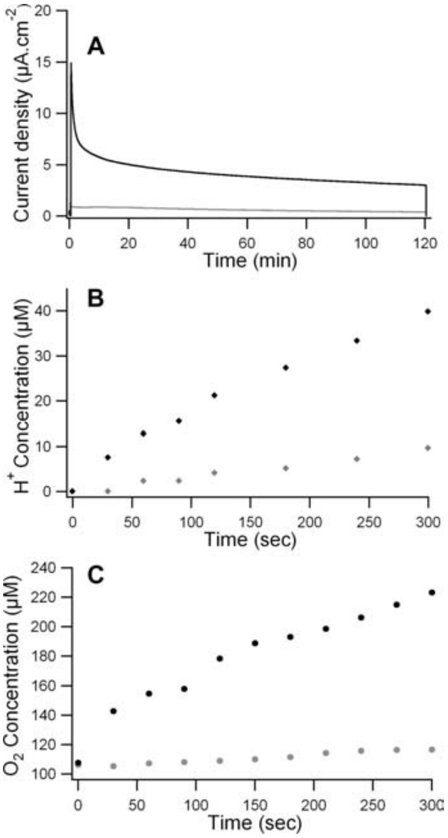

Figure 3. Photocurrent, oxygen and proton generation without external bias for Nafion-coated TiO_2 on FTO (gray) and **1**$^+$-Nafion/**2**-TiO_2 on FTO (black) in H_2O (0.1 M Na_2SO_4); at 22 °C; illumination with white light (290−750 nm), 100 mW/cm^2 for (A) and (B) and 500 mW/cm^2 for (C) These experiments were conducted using independent electrodes. (A) Photocurrent generated on illumination of a 4 mm × 4 mm working electrode for 120 min, commenced after an initial 5 min of peak current testing (not shown). (B) Proton production measured at a 4 mm × 4 mm working electrode in a half-cell separated from the counter electrode by a salt bridge. (C) O_2 generated from a 6 mm × 7 mm working electrode, measured using a Clarke electrode.

Light-driven proton and O_2 production was studied for the **1**$^+$-Nafion/**2**-TiO_2 electrode. When the photoanode was separated from the cathode by a salt bridge, the H^+ concentration in the photoanode half-cell rose to 7 times that observed for TiO_2 alone, over a 5 min period (Figure 3B). Production of O_2 gas was confirmed using a Clarke electrode. Under illumination, substantially more O_2 was produced by **1**$^+$-Nafion/**2**-TiO_2 photoanodes (130 nmol over 5 min) vs TiO_2 alone (18 nmol) (Figure 3C). The measured O_2 yield was found to be within 10% of the yield calculated from the collected charge (0.055 C $\equiv$ 560 nmol of electrons which correspond to the production of 140 nmol of O_2), generated by the **1**$^+$-Nafion/**2**-TiO_2 photoanode. These data, and the 4:1 stoichiometric relationship between photocurrent and O_2, establish that the photocurrent is generated from water oxidation.

The open-circuit voltage of the cell was unstable and close to 0 V, as expected due to the close match of the TiO_2 conduction band and the proton reduction potential at the counter electrode.[4] The generation of hydrogen at the counter electrode was investigated by separating this electrode from the anode using a sealed salt bridge to connect the compartments. The electrolyte was deoxygenated with N_2 and the device illuminated, whereupon photocurrent generation commenced. Production of hydrogen at the counter electrode was subsequently detected using a hydrogen sensor in the headspace above the electrolyte (Figure S2). Thus, the generation of photocurrent from the device corresponds to the production of oxygen gas and protons at the photoanode and hydrogen gas at the cathode (Figure 1B).

Consistent with the spectrum of **2** (λ_{max} ~465 nm)[23] and the photoexcitation profile of **1**$^+$ in Nafion (λ_{max} ~400 nm),[18] a photocurrent was generated on absorption of visible light ($\lambda > 395$ nm, Figure 2). This photocurrent was greatest between 400 and 460 nm, corresponding to excitation of **2**. The peak incident photon to electron conversion efficiency (IPCE, Figure 2B) of 1.7% corresponds to the maximum in the absorption band of **2** (MLCT band).[23]

As noted earlier, initial illumination of the Nafion/**2**-TiO_2 electrodes lacking the cubium (red trace, Figure 2 A) yields a sharp current spike that arises from an initial, but unsustainable, injection of electrons from **2** into the TiO_2 conduction band. A similar spike is observed for the complete **1**$^+$-Nafion/**2**-TiO_2 electrode (blue trace, Figure 2A). In contrast, however, this spike is followed by a second photocurrent peak that develops on a slower (seconds) time scale. This rise in current, seen only in the presence of **1**$^+$-Nafion and water, is consistent with an electron injection from the reduced Mn catalyst, formed by water oxidation, into the oxidized dye molecules (Figure 1B). The slow rise in this second photocurrent indicates that charge transfer between the Mn-cluster/water and oxidized dye is rate limiting. By comparison, in DSSCs a redox mediator rapidly reduces the oxidized dye resulting in sustained turnover and higher currents.

The peak photocurrent generated by **1**$^+$-Nafion/**2**-TiO_2 electrodes (av. 31 μA cm^{-2}) is *ca*. 100 times larger than that of the equivalent untreated TiO_2 films (*av.* 0.32 μA/cm^2) and >10-fold that generated by either the Nafion/**2**-TiO_2 or **1**$^+$-Nafion/TiO_2 electrodes. The dye and catalyst[18] content in a typical cell, estimated as described in the Supporting Information, corresponded to a dye/catalyst ratio of 4.5. The average peak current density (10 cells) of 31 ± 7 μA cm^{-2} corresponds to a turnover frequency (TOF) of 47 ± 10 O_2 molecules cluster^{-1} h^{-1} and 41 ± 9 electrons dye^{-1} h^{-1}, assuming as an overestimate that all molecules in the Nafion film participate in photocurrent generation.[18] The photocurrent generated by a typical **1**$^+$- Nafion/**2**-TiO_2 photoanode was measured over a 2 h period and was found to decrease to just under 10 times the TiO_2 photocurrent over this time (Figure 3A). The charge collected after 2 h equates to 13 O_2 molecules per Mn cluster and 11 electrons per dye molecule, again assuming all molecules participate in photocurrent generation.

Several factors could potentially be contributing to the current decay including desorption of **2** from TiO_2 in the aqueous environment, separation of the Nafion from TiO_2,[18] irreversible ligand substitution, decomposition of the oxidized dye,[25,26] and photodecomposition of the catalyst in light. We have previously shown for the **1**$^+$/Nafion system that catalytic intermediates are susceptible to photodegradation in the absence of applied potential, suggesting that rapid reoxidation of the reduced intermediates contributes greatly to catalyst activity and longevity (>65 h).[18,19] This behavior is analogous to the WOC of PSII, where the S_0 state must be oxidized to S_1 to prevent degradation.[27] Present investigations are focusing on improving device stability by establishing more stable anchoring of the dye and improving electronic communication between the Mn cluster and dye.[28,29]

In conclusion, by matching the electrochemical potentials of the cubium cluster with a suitable photo-oxidizing dye and an electron acceptor (TiO_2) that exhibits low charge recombination, we have been able to couple their respective water oxidation and photoinduced charge separation properties to achieve water oxidation driven solely by light energy. This behavior parallels that of PSII in which charge separation by chlorophyll promotes the oxidation of a catalytic Mn_4Ca core and the subsequent oxidation of water.

Acknowledgment. This work was supported by the Australian Research Council, the US Air Force Office of Scientific Research, a Lemberg Fellowship, an Australian Postgraduate Award, a Monash Publication Award, and a Fulbright Postgraduate Award. The authors thank A. M. Bond, N. Lewcenko, R. J. S. Morrison, U. Bach, and G. Felton for their assistance and valuable comments.

Supporting Information Available: Materials, methods, and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Bockris, J. O.; Dandapani, B.; Cocke, D.; Ghoroghchian, J. *Int. J. Hydrogen Energy* **1985**, *10*, 179–201.
(2) Turner, J. *Science* **2004**, *305*, 972–4.
(3) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37–38.
(4) Gratzel, M. *Nature* **2001**, *414*, 338–344.
(5) Maeda, K.; Teramura, K.; Lu, D.; Saito, N.; Inoue, Y.; Domen, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7806–7809.
(6) Harriman, A.; Pickering, I. J.; Thomas, J. M.; Christensen, P. A. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 2795.
(7) Jiao, F.; Frei, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 1841.
(8) Gratzel, M. *Chem. Lett.* **2005**, *34*, 8–13.
(9) Maeda, K.; Domen, K. *J. Phys. Chem. C* **2007**, *111*, 7851–7861.
(10) Osterloh, F. E. *Chem. Mater.* **2008**, *20*, 35–54.
(11) van de Krol, R.; Liang, Y.; Schoonman, J. *J. Mater. Chem.* **2008**, *18*, 2311–2320.
(12) Kanan, M.; Nocera, D. *Science* **2008**, *321*, 1072–1076.
(13) Youngblood, W. J.; Lee, S. A.; Kobayashi, Y.; Hernandez-Pagan, E. A.; Hoertz, P. G.; Moore, T. A.; Moore, A. L.; Gust, D.; Mallouk, T. E. *J. Am. Chem. Soc.* **2009**, *131*, 926–27.
(14) Cady, C. W.; Crabtree, R. H.; Brudvig, G. W. *Coord. Chem. Rev.* **2008**, *252*, 444–455.
(15) Yagi, M.; Syouji, A.; Yamada, S.; Komi, M.; Yamazaki, H.; Tajima, S. *Photochem. Photobiol. Sci.* **2009**, *8*, 139–147.
(16) Brimblecombe, R.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *Dalton Trans.* **2009**, *43*, 9374–9384.
(17) Ferreira, K. N.; Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S. *Science* **2004**, *303*, 1831–1838.
(18) Brimblecombe, R.; Swiegers, G. F.; Dismukes, G. C.; Spiccia, S. *Angew. Chem., Int. Ed.* **2008**, *120*, 7445–7448.
(19) Brimblecombe, R.; Kolling, D. R. J.; Bond, A. M.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *Inorg. Chem.* **2009**, *48*, 7269–7279.
(20) Dismukes, G. C.; Brimblecombe, R.; Felton, G. A. N.; Pryadun, R. S.; Sheats, J. E.; Spiccia, L.; Swiegers, G. F. *Acc. Chem. Res.* **2009**, *42*, 1935–1943.
(21) Gratzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145–153.
(22) Kuciauskas, D.; Monat, J. E.; Villahermosa, R.; Gray, H. B.; Lewis, N. S.; McCusker, J. K. *J. Phys. Chem. B* **2002**, *106*, 9347.
(23) Pearson, P.; Bond, A. M.; Deacon, G. B.; Forsyth, C.; Spiccia, L. *Inorg. Chim. Acta* **2008**, *361*, 601–612.
(24) Service, R. A. *Science* **2009**, *325*, 1200–1201.
(25) Ogino, I.; Nagoshi, K.; Yagi, M.; Kaneko, M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3431–3434.
(26) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21–36.
(27) Mullins, C. S.; Pecoraro, V. L. *Coord. Chem. Rev.* **2008**, *252*, 416–443.
(28) Liu, F.; Cardolaccia, T.; Hornstein, B. J.; Schoonover, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 2446–2447.
(29) Huang, P.; Magnuson, A.; Lomoth, R.; Abrahamsson, M.; Tamm, M.; Sun, L.; van Rotterdam, B.; Park, J.; Hammarström, L.; Åkermark, B.; Styring, S. *J. Inorg. Biochem.* **2002**, *91*, 159–172.

JA910055A