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Photocatalytic Water Oxidation Using Manganese Compounds Immobilized in Nafion Polymer Membranes

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Abstract

Robust water oxidation catalysts using earth abundant metals are required as part of an overall scheme to convert sunlight into fuels. Here, we report the immobilization of $[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6$ (terpy = 2,2',6',2''-terpyridine), $[\text{Mn}_4\text{O}_6(\text{tacn})_4](\text{ClO}_4)_4$ (tacn = 1,4,7-triazacyclononane), and manganese dioxide nanoparticles in Nafion on fluorine-doped tin oxide conducting glass electrodes. The electrodes are illuminated with white light in the presence of an applied potential and the resulting photocurrent is assigned to the oxidation of solvent water. Photodecomposition of the tetrameric complexes results in a material that is more active for light-driven electrooxidation of water. The reactivity, wavelength dependence, and stability of the compounds in Nafion under illumination are discussed.

Introduction

Light-driven oxidation of water is a vital step in any large-scale scheme to harvest solar energy to produce sustainable fuels.^[1] However, water oxidation is a demanding reaction with a standard potential of 1.23 V versus NHE and requires a suitable catalyst to provide a mechanism for the transfer of four electrons and four protons and for the formation of an O–O bond. A variety of water oxidation catalysts have been developed, including manganese,^[2–4] cobalt,^[5] ruthenium,^[6–9] and iridium^[10,11] compounds as well as both base metal^[12–16] and noble metal^[17,18] oxides.

Although homogenous examples of water-oxidation catalysis allow rigorous mechanistic study, practical considerations for the development of water-oxidation catalysts for use in devices necessitate the immobilization of the catalyst on an electrode surface. Direct contact with the anode allows more efficient electron transfer to the cathode and requires less material than comparative diffusional systems. Furthermore, deposition on an electrode surface is superior for studies using light energy, because the light beam can be focussed on the electrode area. In a system that is to be driven photochemically or electrochemically, the catalytic cycle must be advanced by one electron or one photon steps. This places a design limitation on the development of catalysts intended for solar energy applications.

Recent efforts in our group have focussed on iridium-based water-oxidation catalysts, which can be driven with one-electron oxidants and are, therefore, amenable to incorporation into electrochemical or photochemical systems.^[11,19] Furthermore, we have identified a novel preparation of an iridium oxide water-oxidation catalyst prepared by electrodeposition on an electrode surface from an organometallic precursor.^[20] This compound is highly active with a turnover frequency of 0.6 s^{-1} and may be driven electrochemically with low overpotential.

However, the use of iridium for global scale water oxidation is problematic owing to concerns about low earth abundance, toxicity, and high cost.

Water oxidation is currently achieved on a global scale in plants and cyanobacteria by the enzyme photosystem II (PSII).^[21] The active site of PSII is the oxygen-evolving complex (OEC), containing a Mn_4CaO_5 cluster. The use of manganese is conserved among all known oxygenic photosynthetic species, suggestive of both the sufficient abundance and suitable reactivity of manganese for water oxidation. In the proposed mechanism, four electrons are sequentially removed from the OEC to produce an electrophilic Mn^{IV} -oxyl species, which is attacked by a second substrate water to form dioxygen. The surrounding protein environment encapsulates the OEC in order to regulate efficient electron, proton, and substrate transfer while limiting side reactions.

Although many manganese-based mimics of the OEC have been studied, few are functional water-oxidation catalysts. We have previously reported a homogeneous, multi-turnover manganese water-oxidation catalyst; the $[\text{Mn}_4^{\text{III/IV}}\text{O}_2(\text{terpy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$ (terpy = 2,2';6',2''-terpyridine) complex has been shown to produce dioxygen from water in aqueous solution, but catalytic activity requires the use of two-electron, oxo-donating oxidants.^[2,22] This catalyst has not yet been proven to be suitable for light-driven applications, which require one-electron steps. However, the catalyst does produce oxygen with a single-electron oxidant Ce^{4+} when immobilized in clay, suggesting that encapsulation may be important for advancing the catalyst one electron at a time while maintaining the catalyst in active form.^[23]

One reported manganese-based molecular mimic of the OEC has been oxidatively activated using one-electron steps. The cuboidal $[\text{Mn}_4\text{O}_4(\text{p-MeO-Ph})_2\text{PO}_2]^+$ complex has been demonstrated to produce molecular oxygen at a rate of 20–270 h^{-1} and is reportedly stable for over 1000 turnovers when doped into Nafion, a perfluorinated ion-exchange resin, and illuminated with white light in the presence of a 1.0 V versus Ag/AgCl (1.2 V versus NHE) applied potential.^[4,24,25] However, a recent report has demonstrated that $[\text{Mn}_4\text{O}_4(\text{p-MeO-Ph})_2\text{PO}_2]^+$ is not responsible for the photocatalytic activity. Instead, the manganese complex decomposes under UV illumination to a birnessite-like manganese oxide that was characterized by X-ray absorption spectroscopy.^[26] Nafion has also been employed to prevent bimolecular decomposition of ruthenium catalysts^[27] and to stabilize IrO_2 colloids^[28] for water oxidation. Although the exact structure of the Nafion polymer is not known, the strongly acidic sulfonic acid head groups are envisioned to form negatively charged domains that are able to accept cationic guest complexes.^[29] Furthermore, Nafion has a perfluorinated back-bone, rendering it oxidation resistant, an important feature for use in the highly oxidizing environments required for water oxidation.

Given our recent success in electrodepositing a noble metal catalyst on an electrode surface, we sought to expand our work to surface-bound manganese catalysts. Here, we report the deposition of two manganese tetramers and manganese dioxide on fluorine-doped tin oxide (FTO) conducting glass electrodes. The first manganese compound, $[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2]^{6+}$ (**1**),^[30] is a previously reported manganese tetramer with a 'dimer-of-dimers' topology including two terminal water ligands. The other manganese complex studied in this report is the adamantane-shaped $[\text{Mn}_4\text{O}_6(\text{tacn})_4]^{4+}$ (tacn = 1,4,7-triazacyclononane) complex (**2**).^[31] Neither tetramer has been reported as a water oxidation catalyst in homogeneous solution. Taking inspiration from the work on $[\text{Mn}_4\text{O}_4(\text{p-MeO-Ph})_2\text{PO}_2]^+$, Nafion is used as an immobilizing matrix to hold the manganese compounds near the electrode surface, stabilize reactive intermediates, and aid in proton management, much like the protein environment of PSII. The electrodes are illuminated in the presence of

an applied potential and the resulting photocurrent generated by oxidation of solvent water is measured. The activity of the manganese complexes in Nafion is compared with manganese dioxide, a common decomposition product of high-valent manganese. Our results suggest that the manganese coordination complexes **1** and **2** are rapidly photo-decomposed, leading to the formation of manganese dioxide nanoparticles that are active for water-oxidation catalysis.

Results and Discussion

Deposition of Compounds on FTO

In our continuing studies of **1**, we initially attempted to study catalytic behaviour in the presence of light and an applied potential by adsorbing **1** directly on the surface of FTO glass by evaporation of an acetonitrile solution containing **1**(ClO₄)₆. While the compound did show some photocatalytic behaviour, the photocurrent quickly decayed, suggesting decomposition of the starting compound to an inactive material or diffusion of the compound into the electrolyte solution.

In order to study the deposition of **1** on an electrode surface, a more robust method of maintaining the compound on FTO was needed. We turned to Nafion as an oxidation-resistant, cation-permeable matrix for immobilizing manganese compounds near the surface of FTO electrodes. The manganese complexes were introduced into Nafion and electrodes were assembled by two different methods suited to the properties of each manganese compound. In the case of **2**, a Nafion film was prepared on FTO glass and then immersed in a 2-mM solution of **2** in 80:20 acetonitrile/water. The solubility of **2** in pure acetonitrile is less than 2 mM, but when an aqueous solution was used, very little compound partitioned into the Nafion layer, attributed to the high solubility of the compound in water. An 80:20 acetonitrile/water mixture provided a balance of solubility and doping efficiency. Doping by immersion was not appropriate for **1** because it is not stable in solution for the 12 h required to partition into the Nafion layer. Instead, solid **1**(ClO₄)₆ was mixed with the commercially available Nafion dispersion and then pipetted onto the FTO surface. As heating the film to volatilize the solvents was not possible due to the thermal instability of **1**, the electrodes were allowed to air dry at room temperature. Manganese dioxide electrodes were prepared analogously by first sonicating the nanoparticles with the Nafion dispersion and then pipetting the mixture onto FTO slides. In all cases, doping of the manganese compounds was evidenced by the incorporation of a coloured compound into the otherwise transparent Nafion layer.

Photocatalysis of Manganese Complexes in Nafion

The manganese complexes were tested for water-oxidation catalysis using an electrochemical cell equipped with a quartz window for illumination and arranged in a standard, three-electrode setup. The prepared electrodes were poised at 1.2 V versus NHE, and the dark current then typically equilibrated to a baseline value of 1–4 $\mu\text{A cm}^{-2}$. Although 1.2 V is above the thermodynamic requirement for water oxidation near neutral pH, little reaction occurs due to the large overpotential for the reaction, as evidenced by the low dark current. Upon illumination with white light from a Xe lamp, both complexes showed an increase in current above background that decays rapidly when the light is turned off. Photocurrent, shown for **1** and **2** in Fig. 1, is sustained for the duration of illumination and reversible over several cycles. Typical photocurrent densities above the background are 2–4 $\mu\text{A cm}^{-2}$ for **1** in Nafion and 5–8 $\mu\text{A cm}^{-2}$ for **2** in Nafion. These results are comparable to, although slightly less than, the values observed in the similar system of Brimblecombe et al.^[25] It is difficult to compare the photocurrent densities of the different compounds because the exact concentrations of the compounds in Nafion are unknown;

however, an estimate of the relative amounts of manganese in the Nafion membranes is described below. The photocurrent is attributed to catalytic oxidation of solvent water by high-valent manganese compounds generated by the applied potential and incident light, analogous to the behaviour of $[\text{Mn}_4\text{O}_4(\text{p-MeO-Ph})_2\text{PO}_2]^+$ in Nafion.^[4]

To investigate the requirement for light in photocatalysis, the wavelength range was varied by successive use of long-wavelength-pass filters (Fig. 1). Maximum photocurrent is observed when no filter is applied to the output of the Xe lamp and the spectrum is defined by the 214-nm cut-off of the quartz window. A decreasing photocurrent is observed with longer excitation wavelengths. Some direct excitation of FTO is observed as a background current for wavelengths less than 400 nm; however, photocurrent in the presence of the manganese complexes is greater than background levels at all wavelengths. No photocatalysis is observed at wavelengths greater than 550 nm for either compound, suggesting that high-energy light is required to promote catalysis or generate key catalytic intermediates.

Observation of Photodecomposition

Although the photocurrent densities appeared stable on the electrode surface during several minutes of illumination, much longer stability is required for any practical application to solar fuel production. In order to characterize longer-term stability, compounds **1** and **2** in Nafion were tested by continuous illumination with an applied potential over 16 h. The result is different for the two different manganese tetramers.

The photocurrent for **1** in Nafion is nearly constant at $10 \mu\text{A cm}^{-2}$ over 16 h of illumination (not shown). To further characterize the structural stability of the compound under photocatalysis conditions, the UV-visible absorbance spectra of **1** in Nafion before and after illumination were recorded (Fig. 2). Both pre- and post-illumination spectra show an absorbance band at 330 nm, which is consistent with the absorbance of the terpy ligand in either low-valent Mn^{II} monomeric species or the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ dimer,^[2,32,33] whereas the spectrum of **1** or a $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{IV}}$ dimer would be expected to display an absorbance feature in the 400–500 nm region.^[2,30] If the spectrum is measured within minutes after the electrode is prepared, it is observed that the Mn^{II} or $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ species is formed immediately, and consequently, **1** is not the relevant species during illumination. The formation of lower nuclearity species may proceed through a mechanism similar to the exchange of the μ -oxo ligands of Mn-terpy complexes in which the single μ -oxo breaks but fails to reassemble.^[34,35] However, if $[\text{Mn}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_3]^{2+}$ or $[\text{Mn}_4^{\text{III/IV}}\text{O}_2(\text{terpy})_2(\text{H}_2\text{O})_2]^{3+}$ is doped into Nafion, no photocurrent above background is observed, suggesting that neither of these is the active species. Nevertheless, the spectrum shows little change after illumination except for a decrease in intensity, which may correspond to leaching of a water-soluble manganese compound from Nafion into the electrolyte solution. Although the concentration of the embedded species decreases slightly, no significant decrease of the photocurrent was observed during photoillumination over 16 h. This may be due to the formation during preparation of the electrode of a small amount of stable and catalytically active manganese species, such as manganese dioxide nanoparticles (see below), that are retained within the Nafion layer.

In contrast to the behaviour observed for **1**, photocurrent for **2** in Nafion is observed to increase over the first 3 h from 6 to $17 \mu\text{A cm}^{-2}$ before decreasing slowly over the next 13 h to a final value of $10 \mu\text{A cm}^{-2}$, shown in Fig. 3. During the course of illumination, the qualitative appearance of the Nafion layer changes from dark brown to a lighter, rusty brown (Fig. 4). Together, these observations suggest that **2** has decomposed to a new material during illumination. Notably, the final photocurrent after 16 h of illumination is greater than

the photocurrent during the initial phase, suggesting that the decomposition product is comparatively more active than **2** for photocatalysis.

Intrigued by the discovery of a more active material, we endeavoured to characterize the catalytically active compound by comparing the spectra of the **2**-doped Nafion films before and after illumination. The absorbance spectrum of **2** in Nafion before illumination shows an absorbance feature at 560 nm, which is replaced by a broad absorption band centred at ~400 nm after 16 h of illumination (Fig. 5). Because the spectrum changes significantly, it is not clear whether the same amount of manganese is present before and after illumination; however, evidence of manganese deposition outside the Nafion layer is occasionally observed, which suggests that water-soluble manganese is able to diffuse into the electrolyte solution. The change in the absorbance spectra confirms that decomposition of compound **2** has occurred during illumination, but it is difficult to characterize the product based on UV-visible spectroscopy alone. However, infrared spectroscopy is more diagnostic of the chemical structure. The infrared spectrum of **2** before illumination displays a stretching frequency at 730 cm^{-1} , a characteristic breathing mode of the adamantane-shaped Mn_4O_6 core^[31] (denoted by the arrow in Fig. 5). This signal is not present in the IR spectrum after illumination, indicating that the adamantane-shaped Mn_4O_6 compound has decomposed, although no signature manganese-oxo IR band has replaced the manganese-oxo breathing mode in the resultant material. The other bands present in the infrared spectrum are consistent with Nafion films.^[36]

Manganese dioxide is a known thermal decomposition product of manganese compounds as well as a well known water oxidation catalyst.^[37,38] We compared the spectra of **2** after illumination to authentic nanoparticulate $\alpha\text{-MnO}_2$ in Nafion. Both spectra display a very broad stretch in the $700\text{--}750\text{ cm}^{-1}$ range, but few other diagnostic stretches between 700 and 900 cm^{-1} . The various forms of MnO_2 are known to display characteristic bands in the $400\text{--}700\text{ cm}^{-1}$ range,^[39,40] which is outside the spectral window of our spectrometer. Similarly, the UV-visible spectrum of MnO_2 in Nafion lacks a characteristic absorbance feature, but the normalized post-illumination and authentic MnO_2 spectra shown in the inset of Fig. 5 display a similar shoulder at 400 nm, suggesting that MnO_2 is a possible decomposition product of **2** under illumination. These results are analogous to work on $[\text{Mn}_4\text{O}_4(\text{p-MeO-Ph})_2\text{PO}_2]^+$, in which the molecular precursor is shown to decompose to a manganese oxide material during catalytic cycling under an applied potential with UV illumination.^[26] In this work, the decomposition product is characterized by X-ray absorption spectroscopy and assigned as a disordered $\text{Mn}^{\text{III/IV}}$ oxide that is active for catalysis.

Comparison of the UV-visible spectra of **2** after illumination with MnO_2 allows for estimation of the amount of manganese present in the two layers (Fig. 5). In an example of a typical film, 0.60 mg MnO_2 was added to 0.5 mL Nafion suspension. Then, 5 μL of this solution was pipetted onto the FTO surface and spread over a $0.6 \times 1.0\text{-cm}$ area. Consequently, a typical MnO_2 anode contains $10\text{ }\mu\text{g cm}^{-2}$ MnO_2 . In the UV-visible spectrum, the absorbance of MnO_2 at 450 nm is 0.22. By contrast, the absorbance of Nafion-doped with **2** at 450 nm is 0.75 after illumination. Comparison at 450 nm was chosen specifically because **2** before illumination absorbs minimally at this wavelength. Because the anodes containing MnO_2 and **2** are the same size with approximately the same thickness of Nafion, the amount of manganese in the sample of **2** corresponds to $\sim 34\text{ }\mu\text{g cm}^{-2}$ MnO_2 , indicating that 3.4 times more manganese was introduced by diffusion of the cationic complex into the Nafion membrane than by mechanical incorporation of MnO_2 into the Nafion suspension. Compared with MnO_2 nanoparticles, **2** is both smaller and positively charged, which allows efficient intercalation into the negatively charged domains of the Nafion membrane. This result suggests that the use of a coordination complex as a catalyst

precursor is an effective method for introducing uniformly distributed manganese, which is converted to the active catalyst during illumination and electrooxidation.

Photocatalysis using MnO₂ in Nafion

Because MnO₂ is known to be a water-oxidation catalyst, we prepared FTO electrodes with MnO₂ in Nafion by sonicating nanoparticulate α -MnO₂ with a suspension of commercially available Nafion and then depositing this mixture on FTO glass. The photocatalytic properties, shown in Fig. 6, are similar to those of **1** and **2**. Like the coordination complexes, MnO₂ exhibits sustained, reversible photocurrents. Typical photocurrent density is 18 $\mu\text{A cm}^{-2}$, which is greater than that of either manganese coordination complex. The wavelength dependence of the photocurrent from MnO₂ in Nafion is similar to **1** and **2** when the wavelength range is adjusted by the use of low-pass filters. The highest current density is obtained with no filter ($>214\text{ nm}$), and only small photocurrents are observed with $>550\text{ nm}$ light. This indicates that high-energy light is required to achieve maximum activity. Photocurrent persists for at least 16 h of illumination, indicating that MnO₂ is stable within the polymer framework.

Proposed Role of Light in Photocatalysis

In PSII, visible light photoexcites a special group of chlorophylls called P680, generating a charge separation that forms a highly oxidizing chlorophyll cation radical, which in turn accepts electrons from the Mn₄CaO₅ cluster via a redox-active tyrosine intermediate.^[21] While the mechanism of water oxidation in the OEC of PSII is still a topic of debate, experimental and computational work suggests that, as the manganese cluster is oxidized, one substrate water molecule is successively deprotonated to form a terminal high-valent Mn-oxyl species.^[41] This electrophilic oxygen atom is nucleophilically attacked by the second substrate water to form the O–O bond. Because there are no chlorophylls or other light-harvesting molecules present in the current system to act as photo-sensitizers, the light energy must be playing a different role. However, the O–O bond-forming chemistry is expected to be similar, and, thus, a proposed mechanism should include the formation of a terminal high-valent Mn-oxyl species.

A terminal high-valent Mn-oxyl species could be produced in the systems studied in this work by several possible mechanisms; each proposed mechanism should include the direct excitation of a ligand-to-Mn charge-transfer (LMCT) or Mn-to-ligand charge-transfer (MLCT) band, which is apparently necessary for the activation of these systems. For high-valent manganese complexes, the strong absorption bands in the UV to blue region have been assigned to oxo-to-Mn charge-transfer bands,^[42] so we will focus on LMCT mechanisms. In one possible mechanism, excitation of an LMCT band of the manganese complex results in ligand dissociation, generating a manganese centre with an open coordination site. A water molecule in the surrounding Nafion layer coordinates to the open manganese site, and this species is subsequently oxidized by the applied potential to generate a high-valent Mn-oxyl species. When this state is reached, a second nucleophilic water molecule attacks the electrophilic oxyl species to form the O–O bond. The Nafion polymer network should slow diffusion of the photodissociated ligand, but reassembly of the complex may be a competing process with irreversible decomposition to MnO₂, explaining the build-up of MnO₂ over time. In an alternate mechanism, illumination photolyzes one of the Mn- μ -oxo bonds of the manganese coordination complex to result directly in a terminal high-valent Mn-oxyl species competent for O–O bond formation by nucleophilic attack of water. In this case, the applied potential would be needed to reassemble the Mn-oxo structure by successive oxidations after dissociation of the product oxygen. As in the first mechanism, irreversible formation of MnO₂ could compete with cluster reassembly, resulting in accumulation of MnO₂.

Either mechanism could be extended to manganese dioxide. The photoexcitation of Mn-oxo bonds in MnO_2 could result in the formation of a terminal Mn-oxyl species from surface water molecules or from photolysis of Mn-oxo lattice bonds. Alternatively, light activation may create or activate defect sites on the surface of the manganese oxide particles that are particularly reactive.

Conclusions

We have demonstrated that suspension of manganese coordination compounds and manganese dioxide in an oxidation resistant Nafion matrix is a promising method for developing anodes for water oxidation. The compounds are active in the presence of a 1.2 V applied potential and light, and the resulting photocurrent is assigned to oxidation of bulk water. For both $[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6$ (**1**) and $[\text{Mn}_4\text{O}_6(\text{tacn})_4]^{4+}$ (**2**), photodecomposition of the tetrameric structure is observed under catalytic conditions; however, the resulting material is still active for photocatalysis. MnO_2 , a common decomposition product of manganese complexes under both thermal and photoelectrochemical conditions, is shown to be a competent catalyst for photoassisted electrooxidation of water. Spectroscopic results indicate that MnO_2 is the photodecomposition product of **2**. We conclude that MnO_2 is the active species responsible for the robust photocurrents observed for both coordination complexes **1** and **2**.

Experimental

General Information

$[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6$, $[\text{Mn}_4\text{O}_6(\text{tacn})_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$, and nanoparticulate MnO_2 were prepared as previously reported.^[30,31,43] FTO glass was purchased from Hartford Glass, Inc. Slides were washed with ethanol and allowed to air dry before use. Nafion perfluorinated ion-exchange resin (5% suspension in lower aliphatic alcohols and water) was purchased from Sigma-Aldrich and used as received. Potassium nitrate (Johnson-Matthey, electronics grade) and acetonitrile (J.T. Baker) were used as received. Aqueous solutions were prepared using doubly-deionized water (18.2 M Ω cm). UV-visible spectra were measured with a Varian Cary 50 spectrophotometer by placing the prepared electrode in the beam path. The background spectrum of Nafion on FTO was subtracted. Infrared spectra were measured with a Thermo Nicolet 6700 FT-IR Spectrometer equipped with a SmartOrbit accessory and the background spectrum of Nafion on FTO was subtracted. In the case of either manganese tetramer, the designations **1** and **2** are assumed to refer only to the cationic metal complex without counterion when in Nafion.

Electrode Preparation

Working electrodes were prepared in one of two ways. Method A, used for MnO_2 and $[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6$, involved mixing solid **1**(ClO_4)₆ or sonicating MnO_2 with the Nafion dispersion and then pipetting 5–7 μL of this solution onto a 1.0×0.6 -cm area with edges masked by tape on a 1.3×2.5 -cm slide of FTO glass. The prepared electrode was allowed to air dry. In method B, used for **2**, 5–7 μL of Nafion solution were pipetted onto FTO as in Method A. The electrode was allowed to air dry and then heated in an 80°C laboratory oven for 2 h. The cooled electrode was immersed in a 2-mM solution of $[\text{Mn}_4\text{O}_6(\text{tacn})_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ in 80:20 acetonitrile/water and allowed to stand overnight. Electrodes prepared by either method were rinsed with electrolyte before measurement.

Photoelectrochemical Studies

Electrochemical measurements were made on a Princeton Applied Research VersaSTAT 4 potentiostat/galvanostat using a standard three-electrode system in a vessel equipped with a quartz optical window. A platinum wire was used as the counter electrode, and a 3-M Ag/AgCl electrode (BASi) was used as the reference electrode (NHE versus Ag/AgCl: +0.197 mV). The working electrode prepared as described was placed in the chamber so that the doped Nafion membrane was facing the centre of the quartz window. Unbuffered 0.1 M KNO₃ solution with a pH of ~6.5 was used as the supporting electrolyte. A 300-W Xe light source (Oriel) fitted with a water filter and manual shutter was used as the light source for photochemical experiments. The light intensity at the electrode surface was ~500 mW cm⁻². To avoid temperature fluctuations during lengthy experiments, the photochemical cell was placed in a stirred water bath.

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Fig. 1.

Top: Amperograms of **1** (dashed) and **2** (solid) in Nafion on fluorine-doped tin oxide (FTO) glass, compared with the background (dashed, gray) with an applied potential of 1.2 V versus NHE and illuminated with a Xe lamp. The up-facing arrow indicates light on and the down-facing arrow indicates light off. Bottom: Dependence of photocurrent on wavelength. The label under each peak specifies the filter cut-off wavelength.

Fig. 2.

Absorbance spectrum of **1** in Nafion before and after illumination. The absorption maximum at 330 nm suggests that **1** has decomposed upon introduction into the Nafion film.

Fig. 3. Photocurrent density of $[\text{Mn}_4\text{O}_6(\text{tacn})_4]^{4+}$ (**2**) in Nafion with 0.1 M KNO_3 over 16 h of illumination with a Xe lamp and an applied potential of 1.2 V versus NHE. At 15.5 h, the lamp was turned off and then turned on again.

Fig. 4. Photograph of photoanodes. (a) Nafion film on fluorine-doped tin oxide (FTO) conducting glass. (b) $[\text{Mn}_4\text{O}_6(\text{tacn})_4]^{4+}$ (**2**) doped into Nafion membrane before illumination. (c) **2** doped into Nafion membrane after illumination showing decomposition of starting complex. (d) $\alpha\text{-MnO}_2$ doped Nafion membrane.

Fig. 5.

Top: absorbance spectra of $[\text{Mn}_4\text{O}_6(\text{tacn})_4]^{4+}$ (**2**) in Nafion before (dashed) and after (dotted) illumination and comparison with MnO_2 in Nafion (solid). Inset: Absorbance spectra of **2** in Nafion after illumination (dotted) and MnO_2 (solid), normalized to show the similarity of the two spectra. Bottom: infrared spectra of $[\text{Mn}_4\text{O}_6(\text{tacn})_4]^{4+}$ (**2**) in Nafion before (dotted) and after (dashed) illumination, showing the disappearance of the adamantane breathing mode at 730 cm^{-1} . MnO_2 in Nafion (solid) is shown for comparison.

Fig. 6. Top: amperograms of MnO_2 in Nafion on fluorine-doped tin oxide (FTO) glass (solid line, black), compared with the background (dashed line, gray) with an applied potential of 1.2 V versus NHE and illuminated with a Xe lamp. The up-facing arrow indicates light on and the down-facing arrow indicates light off. Bottom: photocurrents in the presence of long-pass-filtered light. The labels under the peaks specify the filter cut-off wavelength.