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## Polyoxometalate multi-electron transfer catalytic systems for water splitting

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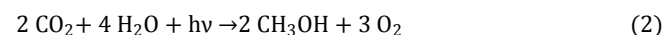
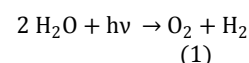
The viable production of solar fuels requires a visible-light absorbing unit, a H<sub>2</sub>O (or CO<sub>2</sub>) reduction catalyst (WRC) and a water oxidation catalyst (WOC) that work in tandem to split water or reduce CO<sub>2</sub> with H<sub>2</sub>O rapidly, selectively and for long periods of time. Most catalysts and photosensitizers developed to date for these triadic systems are oxidatively, thermally and/or hydrolytically unstable. Polyoxometalates (POMs) constitute a huge class of complexes with extensively tunable properties that are oxidatively, thermally and (over wide and adjustable pH ranges)

hydrolytically stable. POMs are some of the fastest and most stable WOCs to date. This Microreview updates the very active POM WOC field, reports the first POM WRCs and initial self-assembling metal oxide semiconductor-photosensitizer-POM catalyst triad photoanodes. The complexities of investigating these POM systems, including but not limited to the study of POM-hydrated metal ion-metal oxide speciation processes, are outlined. The achievements and challenges in POM WOC, WRC and triad research are outlined.

### Introduction

Measurements and models make it ever more certain that the planet will face a serious energy shortage as the availability of economically accessible fossil fuels fails to keep pace with global energy needs.<sup>[1]</sup> Data and analysis also indicate that the environmental change caused by fossil fuel combustion will become increasingly problematic. Although green and alternative energy sources are rapidly becoming more available and less expensive, the net consumption of environmentally worrisome fossil fuel is not dropping significantly. Increases in both global population and average global standard of living paint a less-than-rosy picture for our energy future.<sup>[1b, 1g, 2]</sup> Solar remains the most likely source of sustainable energy for the medium and longer-term future. The other renewable sources of energy, with the arguable exception of biofuels provided the energy production efficiency (photosynthesis and other efficiencies) can be significantly increased, will not likely be sufficient to power the planet. In addition, high density energy will be needed in enormous quantities moving forward; electricity and other sources of energy will not provide sufficient energy density for our major transportation needs (ships, aircraft). Unlike the production of solar electricity, which is a now a rapidly maturing technical area and a major and growing market sector, production of solar fuel is in its infancy.

The principal reactions for the generation of solar fuel are H<sub>2</sub>O splitting to produce H<sub>2</sub> and O<sub>2</sub> (eq. 1) and H<sub>2</sub>O splitting coupled to CO<sub>2</sub> reduction (eq. 2). Technology is needed so both these processes can be driven by terrestrial sunlight and proceed with high rates and selectivity to the desired products. A factor in the slow rates observed for H<sub>2</sub>O oxidation by many systems is that it is a four-electron, four-proton process, hence the need for a catalyst that can facilitate the multiple proton-coupled electron transfer (PCET) processes with low activation barriers.<sup>[3]</sup>



Our group is working on the three requisite areas for solar fuel generation: (1) structures that absorb as much terrestrial sunlight as possible providing long-lived charge-separated excited states; (2) H<sub>2</sub>O reduction catalysts (WRCs) as well as CO<sub>2</sub> reduction catalysts; and (3) water oxidation catalysts (WOCs). The principle vehicles we, and now many other groups are using in the design, study and implementation of these 3 classes of functional structures are polyoxometalates (POMs) because this enormous and growing class of inorganic structures are accessible, tunable, inexpensive and very robust.<sup>[4]</sup> POMs are carbon-free, thus stable to oxidative degradation.<sup>[5]</sup> These metal-oxide-cluster polyanions are capable of accepting multiple electrons for reduction, and transition-metal containing POMs are capable of bearing multiple holes for oxidation. Our research on POM catalysts for multi-electron-processes solar fuel related processes (water oxidation, water and CO<sub>2</sub> reduction) is built on years of work developing and investigating POMs as catalysts for oxidation and other processes.<sup>[6]</sup> There has been and is now extensive research and development on POM catalysts, and several POM-catalyzed processes involving organic substrates have been

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commercialized.<sup>[7]</sup> These cluster polyanions are also stable to thermal degradation and stable to hydrolytic degradation over wide pH ranges that are dictated by the POM framework metals, and the structure of the polyanion unit itself. The POM framework metals range from W(VI), Mo(VI) and V(V), which form acid-stable polyanions to Nb(V) and Ta(V), which form base-stable polyanions.

In this Microreview we discuss two important POM-based WOCs that our group has studied and concerns over the stability of the well studied  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  WOC, as well as recent molecular WOCs with organic ligands. Then, we highlight recent POM-based reduction catalysts and light-to-current-converting POM-containing triadic structures. We have also developed POM-based photosensitizers,<sup>[8]</sup> but do not cover this chemistry here. These areas of research in our group are interlinked as we continue to develop light-driven water splitting based on polyoxometalates.

## WOCs

A major challenge in the development of viable molecular multi-electron transfer catalysts for use in solar fuel applications is their stability both during use and under quiescent conditions. Water oxidation catalysts, in particular, are challenging to develop. Here, we discuss WOCs based on organic ligands and those with POM ligands, and compare shared strengths and weaknesses.

### Molecular WOCs with organic ligands

The last few years have seen a resurgence of interest in all types of WOC, and progress has been dramatic – the maximum reported turnover frequency for molecular WOCs has increased from  $< 1 \text{ s}^{-1}$  five years ago, to values approaching that of the biological OEC. Many groups have reported molecular water oxidation catalysts based on organic ligands since 2010<sup>[9]</sup> and a few are briefly mentioned here. Some notable examples with Ir include  $[(\text{Cp}^*)\text{Ir}(\text{pyr-CMe}_2\text{O})(\text{H}_2\text{O})]^{2+}$ , where  $\text{Cp}^*$  = pentamethylcyclopentadienyl and  $\text{pyr-CMe}_2\text{O}$  = 2-(2'-pyridyl)-2-propanolate, and  $[(\text{Cp}^*)\text{Ir}(\text{H}_2\text{O})_3]^{2+}$ , the former being an authentic molecular WOC and the latter being prone to electrochemical ligand decomposition during water oxidation at an overpotential of 180 mV, to an amorphous carbon containing  $\text{IrO}_x$  film.<sup>[10]</sup> *In-situ* monitoring of the film growth was achieved using an electrochemical quartz crystal nanobalance (EQCN). This decomposition has proved useful in the formation of thin  $\text{IrO}_x$  films.<sup>[11]</sup> The related  $[(\text{Cp}^*)\text{Ir}(\text{L}_2\text{bpy})(\text{H}_2\text{O})]^{2+}$ , where  $\text{bpy}$  = 2,2'-bipyridine and  $\text{L}$  =  $\text{COOH}$  or  $\text{PO}_3\text{H}_2$ , was immobilized on an ITO electrode through the acid (oxy-anion) groups and reported to give stable current densities for water oxidation at an overpotential = 760 mV in pH 4 buffer. In addition,  $[(\text{Cp}^*)\text{Ir}(\text{bpy})(\text{H}_2\text{O})]^{2+}$  was found to be a homogeneous WOC in  $\text{HNO}_3$  with  $\text{Ce(IV)}$  as the oxidant. No ligand oxidation was found and the lack of  $\text{IrO}_x$  film formation was confirmed by EQCN. Unfortunately, the EQCN measurements were performed with the catalyst *in solution* with a gold electrode, thus these measurements do not fully match the catalytic conditions employed in the study (immobilized catalyst on ITO).

A few examples with cobalt are now discussed. When a similar ligand coordination environment is used for cobalt,  $[(\text{Cp}^*)\text{Co}(\text{bpy})(\text{OH}_2)]^{2+}$  acts as a precursor for  $\text{CoO}_x$  through

ligand oxidation during photochemical water oxidation with  $[\text{Ru}(\text{bpy})_3]^{2+}$  as the photosensitizer and  $\text{S}_2\text{O}_8^{2-}$  as the sacrificial electron acceptor.<sup>[12]</sup> The  $\text{Co}^{\text{III}}_4\text{O}_4$  cubane, surrounded and stabilized by different ligands has enjoyed recent success as a molecular WOC, and has been touted as a cobalt analog of the manganese core in photosystem II.<sup>[9e, 9r, 13]</sup>  $[\text{Co}^{\text{III}}_4\text{O}_4(\text{Ac})_4(\text{pyr})_4]$ , the first reported cubane WOC based on cobalt is an authentic molecular WOC, despite the presence of released  $\text{Co}^{2+}(\text{aq})$  from the complex. This behavior contrasts that of ligated  $\text{Mn}_4\text{O}_4$  cubanes, where the observed catalysis could be attributed to metal oxides.<sup>[14]</sup> Another cubane,  $[\text{Co}^{\text{II}}_4(\text{hmp})_4(\mu\text{-OAc})_2(\mu_2\text{-OAc})_2(\text{H}_2\text{O})_2]$ , where  $\text{hmp}$  = 2-(hydroxymethylpyridine) was recently found to catalyze water oxidation with the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$  from pH 5.8 to 8 buffered solution with a maximum TON of 35 at pH 8. No observable ligand oxidation or catalyst decomposition was found by dynamic light scattering, FT-IR (post-catalysis extraction) or UV-vis.

A lot of attention has been given to ruthenium-based molecular WOCs, given that the first one was reported over 30 years ago.<sup>[15]</sup>  $[\text{Ru}(\text{bda})(\text{phthalazine})_2]$ , where  $\text{bda}$  = 2,2'-bipyridine-6,6'-dicarboxylate was reported by Duan et al. to give TONs up to  $\sim 5.5 \times 10^4$  with  $\text{Ce(IV)}$  as the oxidant in triflic acid.<sup>[16]</sup> The authors note that catalyst deactivation occurs, but did not quantify the extent of deactivation, nor address what causes deactivation. Since no quantitative evidence of the stability of this complex was given, the number of catalytic cycles performed by the initial complex is not clear.<sup>[17]</sup>

Finally, copper-based WOCs have begun to appear in the field. Solutions from pH 11.8 to 13.3 which contain simple copper salts and 2,2'-bpy were shown to be electrochemical WOCs at different electrode materials with a 750 mV overpotential.<sup>[18]</sup> The dominant species was found to be  $(2,2'\text{-bpy})\text{Cu}(\text{OH})_2$ , which acts as a homogeneous WOC; no deposits on the electrode were found. The authors could not rule out that a colloidal material was the actual catalyst.

These important studies reinforce a key limitation of such catalysts: organic ligands are oxidatively unstable<sup>[14, 19]</sup> with respect to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . They illustrate that in many, but not all, cases, WOC stability is not being addressed (not quantified under turnover conditions).<sup>[14]</sup>

### POM-based WOCs

To circumvent the inherent oxidative and hydrolytic instability of the organic ligands in molecular water oxidation catalysts (WOCs), our group began to investigate polyoxometalate (POM)-based catalysts in 2006.<sup>[20][21]</sup> All known POM WOCs to date contain redox active d-electron transition-metal active sites where the key steps in the multi-electron (multi-PCET) process of water oxidation occur. POMs with Ru, Co and Ni have been found to catalyze water oxidation by use of chemical oxidants, electrodes, or via photochemical means.<sup>[1h, 13, 21b, 22]</sup> In light of a recent review of the area of POM WOCs,<sup>[1h]</sup> we will only discuss a few POM WOCs here.

**$[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  (“ $\text{Ru}_4\text{POM}$ ”): the first POM-based molecular water oxidation catalyst**

Our investigations of POM-based WOCs started with the diruthenium substituted  $\gamma$ -Keggin POM,  $[\text{Ru}^{\text{III}}_2(\text{OH})_2(\gamma\text{-SiW}_{10}\text{O}_{36})]^{4-}$  ( $\text{Ru}_2\text{POM}$ ).<sup>[21a]</sup> This complex showed a high catalytic activity in water oxidation but was hydrolytically unstable. During our attempts to understand the speciation of this complex, we isolated the dimer of  $\text{Ru}_2\text{POM}$ ,  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  ( $\text{Ru}_4\text{POM}$ ) and discovered its high catalytic activity and stability in water oxidation by  $[\text{Ru}(\text{bpy})_3]^{3+}$  at neutral pH.<sup>[21b, 22b]</sup> At the same time, Sartorel et al. reported the synthesis of  $\text{Ru}_4\text{POM}$  by a different procedure and showed its catalytic activity in water oxidation by  $\text{Ce}(\text{IV})$  under highly acidic conditions.<sup>[22a]</sup> Later this complex was used as a catalyst in a homogeneous visible-light-driven  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$  water oxidation system.<sup>[22c]</sup> This or closely related visible-light-driven systems are now in common use to evaluate WOC activities. The  $\text{Ru}_4\text{POM}$  has been successfully immobilized on different electrode surfaces for

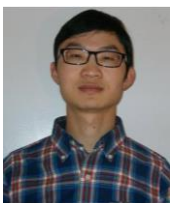
electrocatalytic water oxidation.<sup>[23]</sup> Based on thermodynamic analysis, computational and new electrochemical studies of  $\text{Ru}_4\text{POM}$ , we identified that the intermediate, in which all Ru-atoms are in oxidation state V, is the dominant species forming  $\text{O}_2$ .<sup>[22b, 22d, 22h, 24]</sup> There is no indication of  $\text{Ru}_4\text{POM}$  decomposition in the range of pH between 2 and 12.<sup>[24b]</sup> The WOC chemistry of  $\text{Ru}_4\text{POM}$  has been reviewed in several recent publications<sup>[1h, 13, 25]</sup> and therefore further details are not discussed here.

**$[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (“ $\text{Co}_4\text{POM}$ ”) is a molecular water oxidation catalyst**

The POM water oxidation catalyst  $\text{Co}_4\text{POM}$  is a molecular WOC when used with the chemical oxidant  $[\text{Ru}(\text{bpy})_3]^{3+}$ , as initially



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reported by our group<sup>[22i]</sup> and later verified by others.<sup>[26]</sup> Later, this WOC was used with the oxidant  $\text{ClO}^-$ <sup>[22s]</sup> and in a photochemical system with  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$  and other ruthenium polypyridyl photosensitizers.<sup>[22k, 27]</sup> However, a limit of its use as a molecular WOC was revealed through careful studies by Stracke and Finke.<sup>[28]</sup> This particular POM has been the focus of intense study over the past 3 years,<sup>[22s, 26, 28-29]</sup> as it was the fastest reported POM WOC based on earth-abundant elements (Co, W, P and O) at the time.<sup>[22i]</sup> Since d-electron metal oxides/polyhydroxides themselves can catalyze water oxidation, it is important to account for any amount of the hydrated metal cations (precursors to catalysts) that may exist in solution along with the POM.<sup>[27a]</sup> During the past year, we again reported, and importantly reconfirmed, that  $\text{Co}_4\text{POM}$  is an authentic POM WOC, with both  $[\text{Ru}(\text{bpy})_3]^{3+}$  and with  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$  systems, despite the fact that  $\text{Co}^{2+}(\text{aq})$  is present in solution.<sup>[27a]</sup> To do this, several experiments in addition to the seven in the original (*Science*, 2010) paper that addressed the nature of the actual catalytically active species, were conducted. Some of these experiments should have applicability to homogeneous WOC systems in general. One new line of experimentation was to show that the catalytic activity of twice the amount of  $\text{Co}^{2+}(\text{aq})$  released upon extended aging and that of an equal amount of  $\text{CoO}_x$ , was far lower than the activity of the  $\text{Co}_4\text{POM}$  itself. A second experiment was demonstrating that when twice the amount of  $\text{Co}^{2+}(\text{aq})$  detected (Table 1) was introduced to the catalytic system, no appreciable effect on the  $\text{O}_2$  yield was observed (Figure 1).

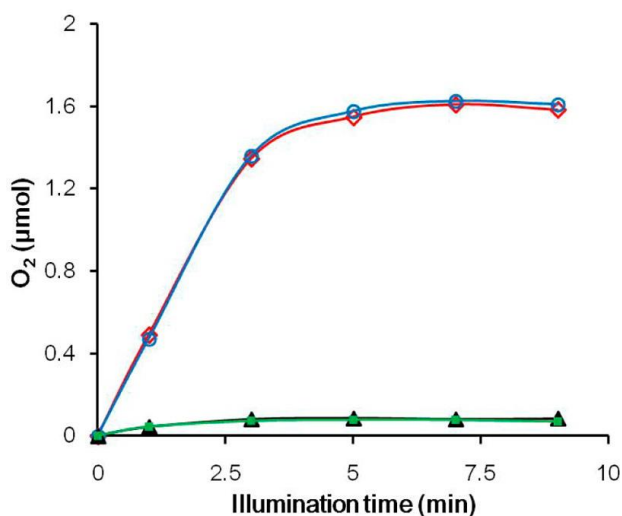


Figure 1. Kinetics of light-driven catalytic  $\text{O}_2$  evolution from water catalyzed by  $\text{Co}_4\text{POM}$  and  $\text{Co}(\text{NO}_3)_2$ . Conditions: 455 nm light emitting diode (17 mW, beam diameter  $\sim 0.5$  cm), 5.0 mM  $\text{Na}_2\text{S}_2\text{O}_8$ , 1.0 mM  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 2.0  $\mu\text{M}$   $\text{Co}_4\text{POM}$  (blue), 2.0  $\mu\text{M}$   $\text{Co}_4\text{POM}$  + 0.15  $\mu\text{M}$   $\text{Co}(\text{NO}_3)_2$  (red), 0.15  $\mu\text{M}$   $\text{Co}(\text{NO}_3)_2$  (black) all in 120 mM sodium borate buffer, and 0.15  $\mu\text{M}$   $\text{Co}(\text{NO}_3)_2$  (green) in 80 mM sodium borate buffer. Initial pH = 8.0, total volume 2.0 mL. Reproduced with permission from reference<sup>[27a]</sup>. Copyright 2013 American Chemical Society

In addition to reporting the kinetics of oxidant consumption and  $\text{O}_2$  yields with  $\text{Co}^{2+}(\text{aq})$  and  $\text{CoO}_x$  catalysts, we used a new POM extraction method,<sup>[27a]</sup> based on earlier work,<sup>[30]</sup> which quantitatively removes  $\text{Co}_4\text{POM}$  from the aqueous layer and transports it to an organic solvent (typically toluene) layer. The extraction leaves all other components in the system (essentially all the  $\text{Co}^{2+}$  and insoluble cobalt hydroxides / oxides) in the aqueous layer. This enabled us to measure the catalytic activity of the

remaining species formed prior to, during or after catalytic water oxidation. The result of extraction of  $\text{Co}_4\text{POM}$  from a pH 8.0 80 mM sodium borate buffer solution containing 5.0 mM  $\text{Na}_2\text{S}_2\text{O}_8$  and 1.0 mM  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  is dramatic: the  $\text{O}_2$  yield is negligible post extraction. If  $\text{Co}_4\text{POM}$  is added back to the same solution, the  $\text{O}_2$  yield matches, within experimental error, that from an unmodified solution. The POM extraction technique will aid other researchers studying POM WOCs to distinguish them from other possible species that might be simultaneously present and catalytically active.

#### When $\text{Co}_4\text{POM}$ and a related POM are not molecular water oxidation catalysts

In contrast,  $\text{Co}_4\text{POM}$  and a related POM,  $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ ,  $\text{Co}_9\text{POM}$ , are not stable when used *in solution* as electrochemical water oxidation catalysts. This behavior establishes an important limit on the use of multi-cobalt POM WOCs. Not only is  $\text{Co}^{2+}(\text{aq})$  released from the POMs, but the observed catalytic water oxidation activity in the system is the result of this released  $\text{Co}^{2+}(\text{aq})$ . When  $[\text{Co}_4\text{POM}] = 0.5$  mM at an overpotential = 580 mV and when  $[\text{Co}_9\text{POM}] = 1.0$  mM at an overpotential  $\approx 600$  mV, the amount of  $\text{Co}^{2+}(\text{aq})$  released during electrolysis is responsible for forming the actual catalyst ( $\text{CoO}_x$ ). When  $[\text{Co}_4\text{POM}] = 2.5$   $\mu\text{M}$ , the electrocatalytic activity of the POM at overpotential  $\geq 600$  mV is indistinguishable from that of the observed amount of  $\text{Co}^{2+}(\text{aq})$  released from the POM during the course of the experiment. While these studies define limits of stability and use of homogeneous water oxidation catalysis by multi-cobalt POMs, they do not detract from the overwhelming evidence that these POMs are molecular WOCs when used with chemical oxidants. That is, the exact conditions where the POMs serve as catalysts or as precursors to metal oxides are important when comparing them. These same issues pertain to all homogeneous WOCs, including those addressed above with organic ligands.

#### Towards a better understanding of the complex equilibria associated with $\text{Co}_4\text{POM}$

So far, studies on this POM have focused on how buffer, pH, concentration and type of oxidant used control the catalytic activity in the system and the catalyst identity under different sets of conditions. Our group found that both the catalytic activity and stability of  $\text{Co}_4\text{POM}$  strongly depend on pH and buffer identity. For example, the amount of  $\text{Co}^{2+}(\text{aq})$  released from the parent POM after extended aging depends on the identity of the buffer (Table 1) and is one factor that describes the stability of the parent POM. It is likely that related POM WOCs, such as  $\text{Co}_9\text{POM}$  would show a similar buffer dependence, but no studies have addressed this to date.

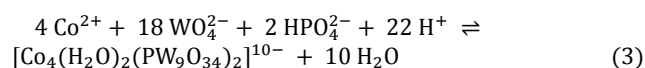
Table 1. Amount of  $\text{Co}^{2+}(\text{aq})$  detected upon aging  $\text{Co}_4\text{POM}$  in various buffers.

Buffer	$\text{Co}^{2+}(\text{aq})$ detected ( $\mu\text{M}$ ) <sup>[a]</sup>
sodium phosphate	$0.44 \pm 0.02$
sodium borate	$0.07 \pm 0.01$

[a] 2.0  $\mu\text{M}$  of  $\text{Co}_4\text{POM}$  was aged in 80 mM of pH 8.0 buffer for 3 hours. The POM was extracted, and then the amount of  $\text{Co}^{2+}(\text{aq})$  remaining in the buffered water was quantified by inductively coupled plasma mass spectrometry.



However, it would be more helpful to understand the mechanism by which these POM WOCs equilibrate, so that one could rationally design new POM WOCs that are more stable to loss of the d-electron metal centers (or have equilibria where the metal is more stable in the POM rather than metal hydroxide/oxide). Recall that POMs themselves constitute dynamic systems and once in solution will equilibrate as governed by the law of mass action. This means, in the case of Co<sub>4</sub>POM, its equilibrium concentration is strongly dependent on [H<sup>+</sup>], [WO<sub>4</sub><sup>2-</sup>], [HPO<sub>4</sub><sup>2-</sup>] and [Co<sup>2+</sup>] (eq. 3) and its formation from these components and that of related POMs is extremely dependent on the ratio of Co:X:W, where X = POM heteroatom.<sup>[31]</sup>



Likewise, slight variation in these concentrations, for example if the POM is placed in a buffer, acts as a driving force to partially decompose the POM. Indeed, Stracke and Finke noted that no observable (quantifiable) change in the UV-vis spectrum of 500 μM Co<sub>4</sub>POM in 0.1 M LiClO<sub>4</sub> occurs over a three-hour period. In marked contrast, Stracke and Finke noted the slow loss of Co<sub>4</sub>POM due to the release of Co<sup>2+</sup>(aq) in buffer solutions at pH 8.0,<sup>[28]</sup> which we confirmed and showed occurs up to pH 10.0.<sup>[27a]</sup> Our group found that this decomposition process is accelerated in sodium phosphate buffer, which may be the result of the formation of insoluble Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, which has a K<sub>sp</sub> = 2.05 × 10<sup>-35</sup>.<sup>[32]</sup> To date, this species has not been isolated from a system containing Co<sub>4</sub>POM in sodium phosphate buffer.

Measurement of the equilibrium association constants for the metal, e.g. Co<sup>2+</sup>(aq), in the POM ligands (K<sub>eq</sub> values) is the logical first step towards understanding the complex equilibrium of these POMs. However, as correctly noted by Stracke and Finke,<sup>[28a]</sup> this has only been done so for non-WOC POMs. These numbers could support the formation of the proposed [Co<sub>3</sub>Na(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>11-</sup>, suggested as a possible species that forms when 1.0 μM Co<sub>4</sub>POM is electrolyzed at ≥ 1.3 V (vs Ag/AgCl) in 0.1 M pH 8.0 sodium phosphate buffer.<sup>[28b]</sup> However, this route is unconfirmed, in part, because polytungstates equilibrate slowly, the exact species present are difficult to detect/quantify and the decomposition pathway

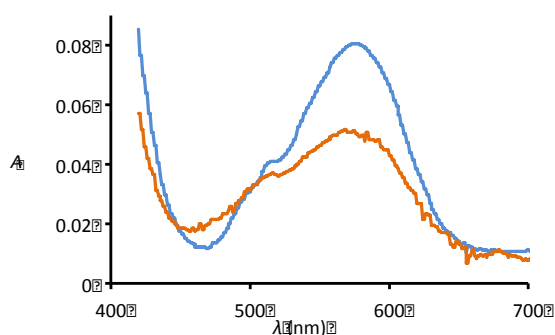


Figure 2. The UV-vis spectra of 0.5 mM Co<sub>4</sub>POM in 80 mM pH 8.0 sodium borate buffer before (blue) and after (orange) aging for 10 hours at 60 °C.

is unknown. Therefore, during the course of a catalytic experiment (period of minutes) the POM never achieves true equilibrium. The only species that we have direct evidence for and can quantify are Co<sub>4</sub>POM and Co<sup>2+</sup>(aq). Under quiescent conditions in the presence

of buffer, we observe a slow, pH-dependent release of Co<sup>2+</sup>(aq) over a three-hour period for this POM, again suggesting that equilibrium for this process favors the POM. Aging experiments at room temperature for up to 12 hours continue to show a slow loss of Co<sub>4</sub>POM; even upon heating the system (solution) to 60 °C for 10 hours fails to drive the system to full equilibrium (Figure 2). At this time, we cannot not identify by UV-vis, all of the products that form after heating or aging the solutions for long periods of time (Figure 2), and therefore are unable to calculate equilibrium association constants, or K<sub>eq</sub>.<sup>[27a]</sup> Developing a handle to identify the specific POM species present would greatly aid design of new POM WOCs.

## POM-catalyzed multi-electron reduction reactions

Several features of natural photosynthesis are typically modelled in the reduction or fuel-forming unit as well the light absorption-charge separation and water oxidation units in artificial photosynthetic systems. Reductive equivalents are generated by light irradiation coupled with redox cycles in Photosystems I and II. The promise of efficient and sustainable photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> has inspired researchers to develop promising heterogeneous<sup>[9], [33]</sup> and homogeneous<sup>[33b], [34]</sup> photocatalysts for the reaction. Ideally, these photocatalysts would be coupled with WOCs in order to develop light-driven water splitting systems.

Photocatalysis based on dispersion of heterogeneous semiconductor particles continues to offer promise because these particles are frequently quite robust under strong light illumination, readily prepared and many are low cost.<sup>[33b], [33d], [35]</sup> Nevertheless, it is important to control the chemical conversion processes at the molecular level and to easily study them both experimentally and computationally at this level in order to achieve highly efficient catalytic cycles like those in nature.<sup>[36]</sup> There is a plethora of noble-metal-based catalysts<sup>[37]</sup> and/or chromophores<sup>[34c], [38]</sup> whereas, systems based exclusively on earth-abundant elements continue to be few in number.<sup>[34b], [39]</sup> Since POMs are capable of accepting multiple electrons, their use as H<sub>2</sub>O and/or CO<sub>2</sub> reduction catalysts is logical, however there are few examples of noble-metal-free POM water reduction catalysts (WRCs).

## Reduced POMs as WRCs

Reduced POMs,<sup>[40]</sup> typically generated by UV irradiation in the presence of organic substrates,<sup>[41]</sup> have long been known to slowly evolve H<sub>2</sub> in acidic aqueous media. After early reports,<sup>[40], [42]</sup> and the demonstration by Darwent that Pt(0) could catalyze the reoxidation of reduced POMs,<sup>[41]</sup> several studies on UV-light-induced photooxidation of organic substrates catalyzed by various POMs with simultaneous H<sub>2</sub> evolution catalyzed by Pt(0) were published.<sup>[6a], [42-43]</sup>

None of these initial studies reported high rates of H<sub>2</sub> evolution in the absence of Pt(0). One exception is POM-modified carbon electrodes that electrochemically reduce protons to H<sub>2</sub> reported by Nadjo, Keita and coworkers in the mid 1980s and early 1990s. However, the actual catalyst in these systems was never fully identified<sup>[44]</sup> and these systems do not utilize light. Clearly, the development of cheap, readily available, visible-light-response and abundant-metal-based systems as a substitute for noble metals is a

general challenge in catalyzed multi-electron processes and a major goal in artificial photosynthesis. Recently, Artero, Proust and coworkers<sup>[45]</sup> developed a covalent-linked Ir(III)-photosensitized POM complex, which shows very efficient photoreduction of a polyoxometalate in the presence of sacrificial electron donor upon visible light irradiation. Photocatalytic H<sub>2</sub> production proceeds without obvious loss of activity for more than one week; however, a TON of only 41 is obtained after 7 days of irradiation.<sup>[14]</sup>

### A noble-metal-free POM-based WRC

In an effort to develop hydrolytically stable, more efficient and noble-metal-free molecular water reduction catalysts (WRCs), our group started systematically evaluating the large experimental space defined by suitable families of POMs, and recently reported visible-light-driven hydrogen evolution from water catalyzed by a tetra-manganese-containing POM, Na<sub>10</sub>[Mn<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(VW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] (Mn<sub>4</sub>POM).<sup>[46]</sup> Steady-state and time-resolved fluorescence decay studies confirm the oxidative quenching of [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup> (the <sup>3</sup>MLCT excited state) by Mn<sub>4</sub>POM. The resulting reduced form of the catalyst reacts with water, confirmed by isotope labeling experiments, to generate H<sub>2</sub>. Under minimally optimized conditions, a TON of 42 was obtained after 5.5 h of irradiation. Although its present efficiency is higher than the Ir(III)-photosensitized POM catalyst,<sup>[14]</sup> it is still too low for practical use. The longer-term stability of Mn<sub>4</sub>POM was assessed by UV-vis under quiescent conditions for 21 h, which found only a 1% decrease in absorbance due to the POM. FT-IR analysis of the catalyst isolated after an extended period of irradiation (24 h) confirmed that the POM is intact, although this is not a quantitative measure of its stability. Our group is currently targeting mono-/multi-transition-metal-containing but noble-metal-free POM catalysts for the reduction of H<sub>2</sub>O and CO<sub>2</sub> under either electrocatalytic and photochemical conditions. By carefully tailoring the electronic structures, more viable (fast, selective and stable) POM WRCs and CO<sub>2</sub> reduction catalysts should be identified.

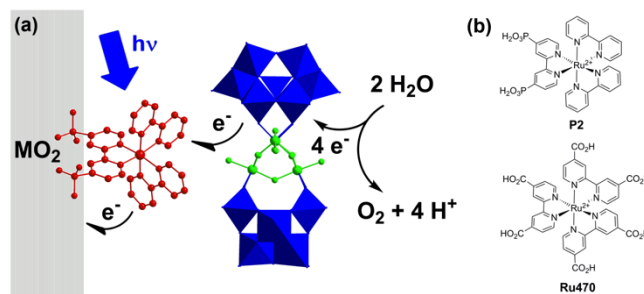
### Polyoxometalate WOC functionalized photoanodes

Studies of polyoxometalate-based water oxidation photoanodes have so far been limited. These studies have focused on “triads” consisting of n-type semiconductor metal oxides (TiO<sub>2</sub>, SnO<sub>2</sub>), ruthenium-based sensitizer dyes, and [{Ru<sub>4</sub>O<sub>4</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>}(γ-SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]<sup>10-</sup> (Ru<sub>4</sub>POM) catalyst.<sup>[47]</sup>

These systems are essentially POM-containing analogs of other dye-sensitized water oxidation photoanodes published in the last five years<sup>[48]</sup> and as such, their operating principle is similar to that of the dye-sensitized solar cell (DSSC) – electrons are injected from the sensitizers into the TiO<sub>2</sub> conduction band (Scheme 1).

However, instead of regeneration by a redox mediator, the oxidized sensitizers take electrons from the catalyst, which in turn oxidizes water. In POM triad studies, Ru<sub>4</sub>POM, despite its lower speed, has been the catalyst of choice for three reasons. Firstly, its strong UV-vis absorption provides a handle allowing straightforward quantification of its presence on the electrode surface. Secondly, it has a wider pH range of activity (and stability) in aqueous media than most POM WOCs reported thus far. Lastly, as discussed above, the triad system would subject

multi-cobalt POMs to conditions that facilitate their decomposition (i.e. high electrochemical bias). However, a water insoluble salt of Co<sub>9</sub>POM does appear to be stable in a carbon paste anode.<sup>[22v]</sup>



Scheme 1. (a) Principle operation of a triadic water oxidizing photoanode incorporating Ru<sub>4</sub>POM. (b) Structures of the **P2** and **Ru470** dyes which have been used in triads with Ru<sub>4</sub>POM.

The first study of Ru<sub>4</sub>POM at a dye-sensitized electrode was performed by Bonchio, Scandola *et al.*<sup>[47a]</sup> This nanosecond flash photolysis study on TiO<sub>2</sub>-[Ru(bpy)<sub>2</sub>(dpbpy)]<sup>2+</sup> (**P2**)-Ru<sub>4</sub>POM, where dpbpy = 2,2',bipyridine-4,4'-dicarboxylate, indicated that the bleach resulting from photooxidation of the dye recovered significantly faster in the presence of the catalyst, suggesting electron transfer to the oxidized dye. Subsequently, we investigated Ru<sub>4</sub>POM at TiO<sub>2</sub> using the carboxylate binding dye Ru470, with fs to ns visible transient absorption spectroscopy which indicated accelerated bleach recovery on this faster timescale.<sup>[47b]</sup> Our most recent and comprehensive study returned to the phosphonate-binding **P2** system,<sup>[47c]</sup> due to its superior resistance to hydrolysis, and investigated SnO<sub>2</sub> and ZrO<sub>2</sub> in addition to TiO<sub>2</sub>. Importantly, ultrafast transient IR measurements confirmed that electrons were still injected into TiO<sub>2</sub> in the presence of the catalyst, and visible transient measurements on the ZrO<sub>2</sub> control (which cannot accept electrons from the **P2** excited state) eliminated a dye-catalyst quenching phenomenon as the major source of the bleach recovery. Half-lifetimes for the

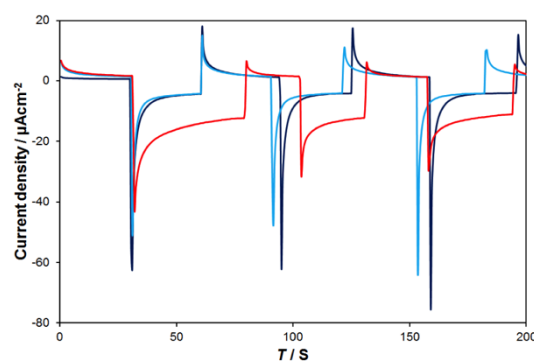


Figure 3. Photoelectrochemical measurements (chronoamperometry) of TiO<sub>2</sub>-**P2** (dark blue), TiO<sub>2</sub>-**P2**-Zn<sub>4</sub>POM (light blue), and TiO<sub>2</sub>-**P2**-Ru<sub>4</sub>POM (red) films at an applied bias of 0 mV vs Ag/AgCl, pH 5.8. Reproduced with permission from reference.<sup>[47c]</sup> Copyright 2013 American Chemical Society

recovery of oxidized **P2** of 127 ps (on TiO<sub>2</sub>) and 520 ps (SnO<sub>2</sub>) were established: these are significantly faster than regeneration of Ru-polypyridyl dyes by I<sup>-</sup> in the DSSC,<sup>[49]</sup> and around 6 orders of

magnitude faster than those from IrO<sub>2</sub> to related sensitizers.<sup>[50]</sup> Furthermore, evidence was seen for the persistence of TiO<sub>2</sub>(e<sup>-</sup>)-P2-Ru<sub>4</sub>POM(h<sup>+</sup>) excited states beyond 0.5 μs. In principle, this rapid electron transfer and long-lived charge-separated state is very encouraging for the use of these systems in light-driven water oxidation. Indeed, significant (100%) photocurrent enhancements (Figure 3) are observed when Ru<sub>4</sub>POM is added to TiO<sub>2</sub>-P2 at pH 5.8 – such enhancements are not achieved with the inactive POM, [Zn<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> (Zn<sub>4</sub>POM), or in the absence of water, suggesting oxidation of water was the source of the photocurrent. However, the quantum efficiency (ca. 0.2%) is significantly lower than that for the related IrO<sub>2</sub>-based system described above,<sup>[48a]</sup> and nearly two orders of magnitude lower than that recently achieved for triads based on a super-fast, Ru bipyridine dicarboxylic acid complex.<sup>[48e]</sup> Given the favourable electron transfer dynamics described above, it appears that replacing Ru<sub>4</sub>POM with a faster POM WOC is the key to developing higher performance POM-functionalized photoanodes.

We will shortly report in more detail on O<sub>2</sub> evolution, and the stability of these triadic systems. Despite their apparent promise, however, they suffer from two important Achilles' heels when it comes to stability: oxidation of the dye, and desorption of both dye and catalyst. Both of these tend to become more severe in the pH > 7 range where POM catalysts are most active. While many steps may be taken to mitigate these problems, such as use of polymerized dyes,<sup>[51]</sup> completely overcoming them is likely to require alternative, purely inorganic, light-absorbing supports. Importantly, no results obtained thus far indicate that POM WOC stability is the success limiting factor in the triadic systems.

## Conclusions

The synthesis, X-ray structures, spectroscopic properties and catalytic activity of many polyoxometalate (POM) water oxidation catalysts (WOCs) and some water reduction catalysts (WRCs) have now been reported. On the reduction side, only a few examples of noble-metal-free POM water reduction catalyst exist, but there is vast potential for their continued development, including incorporation into photocathodes. POM WOC immobilization on a range of carbon-based and metal oxide supports has been achieved and the properties of these dyadic systems have been elucidated using various approaches and techniques. One limitation to viable triads is photosensitizer degradation and viable inorganic analogues are not yet available. However, POM WOCs, unlike coordination compounds, are carbon-free and thus thermodynamically stable with respect to oxidative degradation; they are thermally stable and also hydrolytic stable over wide pH ranges that vary with the POM ligand structure, the active-site d-electron metals, and solution parameters. One solution parameter that has impacted publications to date is the use of phosphate containing buffers. Phosphate should be avoided because it inhibits water oxidation and cobalt phosphate is thermodynamically more stable hydrolytically at neutral and basic pH values than the cobalt-containing POMs.

A central challenge, not just with POM WOCs, but essentially all molecular WOCs, is to establish the amount of different species present that are catalytically active for water oxidation under turnover conditions. Nearly all literature studies of homogeneous WOCs note decomposition of the WOC during turnover, and

sometimes note that metal oxide (typically RuO<sub>2</sub> from oxidative followed by hydrolytic decomposition of Ru-based coordination compound WOCs) is a likely decomposition product of the initial catalyst that forms during turnover. These studies, however, do not quantify the amount of hydrated metal cation that forms from the initial molecular WOC during turnover nor the amount of metal oxide WOC that forms from the metal cation during catalysis. Therefore, the amount of water oxidation that arises from transient hydrated metal cations or subsequently forming metal oxide particles is unknown. Additional detailed studies on these decomposition pathways for all WOCs could facilitate development of more robust catalysts.

Since nearly all molecular water and CO<sub>2</sub> reduction catalysts are ultimately susceptible to hydrolytic degradation, the development of POM catalysts for these reductions is of considerable interest: POMs can be formulated to be thermodynamically stable to hydrolysis over wide pH ranges in aqueous media. Thus far the rates of these reductions are very slow. However, many parameters have yet to be examined and optimized. One must note in the parallel study and development of POM WOCs in our laboratory over the last 5 years that the water oxidation / O<sub>2</sub> evolution rates of these systems have increased 10,000-fold or more through systematic and targeted variation of the POM compositions and structures. The same situation may apply for the development and optimization of POM reduction catalysts.

Finally, it is clear from the early research thus far that POMs can function as effective WOCs in triadic systems. The lifetimes of these systems under operating (turnover) conditions is not dictated by POM decomposition but rather by dye (photosensitizer) decomposition and hydrolytic displacement of the dye off the semiconductor metal oxide electrode surface.

## Acknowledgments

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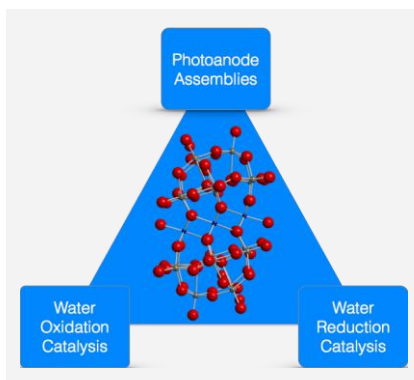
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## Layout 1:

Polyoxometalates (POMs) have enjoyed recent success as catalysts in the multi-electron water oxidation and reduction reactions. They have also been incorporated into photoanodes for heterogeneous water oxidation. We address the challenges that remain and highlight upcoming advances in the field.



### Key Topic

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Polyoxometalate multi-electron transfer catalytic systems for water splitting

Keywords: Polyoxometalates / Water Splitting / Photochemistry / Supported Catalysts



