

Cite this: *Chem. Soc. Rev.*, 2012, **41**, 7572–7589

www.rsc.org/csr

## CRITICAL REVIEW

## Polyoxometalate water oxidation catalysts and the production of green fuel†

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Received 30th July 2012

DOI: 10.1039/c2cs35292c

In the last five years and currently, research on solar fuels has been intense and no sub-area in this field has been more active than the development of water oxidation catalysts (WOCs). In this timeframe, a new class of molecular water oxidation catalysts based on polyoxometalates have been reported that combine the advantages of homogeneous and heterogeneous catalysts. This review addresses central issues in green energy generation, the challenges in water oxidation catalyst development, and the possible uses of polyoxometalates in green energy science.

## 1. Introduction

### 1a. General challenges in green fuel production

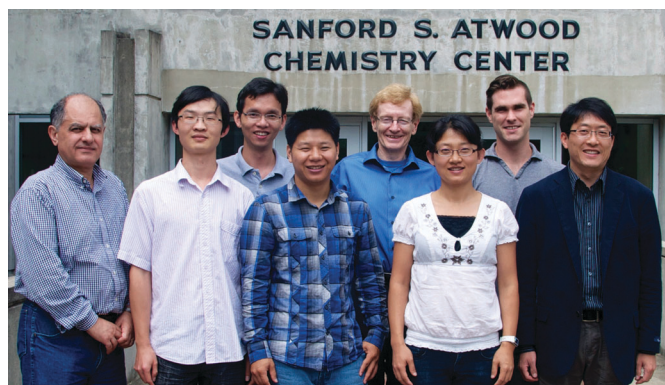
There are multiple current and growing concerns with respect to generation, storage and utilization of energy on a global scale.<sup>1–4</sup>

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† Part of a themed issue covering the latest developments in polyoxometalate science.

Trends in planetary consumption of energy track with population growth and standard of living, and all these parameters are rapidly increasing. While there remain vast reserves of fossil fuels (gas, liquid and solid) those that are technologically and economically accessible are rapidly diminishing. Thus projections are that we could run out of inexpensive fossil fuel energy in the near future.<sup>5–7</sup> Furthermore, it is the consensus of the research community (major reports by the US National Academy of Sciences and other organizations of truly credible investigators) that global climate change, and not just the increase in carbon dioxide by 100 parts per million in the last few decades, is real and caused in good



From left to right: Djamaladdin G. (“Jamal”) Musaev (Director of the Emerson Center for Scientific Computation), Hongjin Lv (PhD student of Prof. Hill), Chongchao Zhao (PhD student of Prof. Hill), Zhen Luo (postdoctoral fellow with Prof. Hill), Craig L. Hill (Goodrich C. White Professor), Guibo Zhu (PhD student of Prof. Hill), James W. Vickers (PhD student of Prof. Hill), and Jie Song (former PhD student and postdoctoral fellow with Prof. Hill). Missing: Yurii V. Geletii (Senior Scientist with Prof. Hill) and Tianquan Lian (William Henry Emerson Professor). All are currently at Emory University.

*Craig L. Hill (correspondence author) studies complex materials, including a range of catalysts, multi-functional nano structures, and inorganic clusters. The group also investigates reaction mechanisms and is partly focused now on several multidisciplinary problems associated with green energy production.*

measure by our civilization's use of fossil fuels.<sup>8</sup> Fortunately, the elected leaders of nearly all countries, both developed and developing, are listening to the research community and commensurate actions have been initiated to combat these dual and linked concerns of energy availability and environmental preservation. These range from initiatives on energy conservation and high mileage cars<sup>9–11</sup> to substantial funding for green (non-CO<sub>2</sub> producing, *etc.*) energy in nearly all countries with research establishments.

At present, fossil fuels dominate energy resources in nearly all countries, with nuclear fission next most important.<sup>12,13</sup> Nuclear energy constitutes about 9% of the energy generated and used in the United States and a similar percentage is seen in some other developed countries. France is the principal outlier in this context deriving much of their domestic energy from nuclear fission. Nuclear energy, like fossil fuel energy and to lesser extent all the other sources of energy, are subject to a host of national and local issues, and these change with time. Although nuclear fission does not produce greenhouse gases it does create waste whose safe and effective long-term disposal still defines some challenges.<sup>14</sup>

Nuclear fusion holds the promise for an inexhaustible source of energy to power the planet.<sup>15,16</sup> This is not an area of expertise of our co-author team, so we limit our comments to the fact that considerable investment in this area has produced advances and the multiple approaches can point to some promising findings. Nonetheless, this research community is not close to viable solutions including the nuclear fusion reactors themselves at present. If the formidable existing technical problems can be surmounted there also remains the challenge of dealing with the astronomical costs that many working nuclear fusion reactors would necessitate.

The stark realities noted above associated with fossil fuels, nuclear fission and nuclear fusion energy has lead inevitably to careful evaluation of the renewable sources of energy. The most prominent of these are hydroelectric, geothermal, wind, tides, ocean thermal energy conversion (OTEC), and solar. At present in most countries, all these renewable energy generation technologies together constitute only a small percentage of the total energy production pie chart. Recent substantial increases in governmental and other research support with commensurate levels of research activity (very high) and other factors are resulting in many small breakthroughs in the advancement and effective implementation of these technologies. While the energy derived from all these renewable sources is increasing rapidly, progress is still modest and projections for the total production of renewable energy is well below what it needs to be to meet the projected energy shortages coming in the next decades.

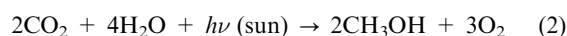
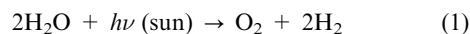
The only renewable source of energy with sufficient capacity "to power the planet" is solar.<sup>2,17</sup> The challenges encountered with all the above renewable energy sources have been well elaborated in recent expositions, and we refer the reader to some of these works.<sup>1–4</sup> There are technical, production, distribution and other challenges to the use of all the renewables but the overriding issue is the one of capacity. All the renewables, at reasonable projected maximal uses do not have sufficient energy to power the planet given demographic and other trends.

The density of energy is a central issue that permeates both the research and practice of energy production and energy storage.

It is a central variable in the all the renewable energy technologies, and it impacts potential uses for polyoxometalates (POMs) in the energy sector. Energy can be stored in many ways ranging from thermal radiance, such as fire-heated boulders dating back to prehistorical times, to electricity and fuel, the energy forms of greatest utilization and focus currently. The advances in electricity generation and storage have been substantial in recent years and currently. Solar electricity from photovoltaic (PV) systems has been getting rapidly cheaper in the last few years spurred on by global competition in the private sector and rapidly increasing markets.<sup>18–20</sup> Likewise, electricity storage, *i.e.* battery technology, has been getting markedly better,<sup>21</sup> particularly with introduction of new nanostructured materials.<sup>22</sup> Even the most advanced batteries, however, have energy densities that are far too low for many high demand needs. Given that a great percentage of the global economy depends on shipping and a good deal depends on air transportation, there is a clear need for technology to facilitate the production of enormous quantities of renewable fuel.

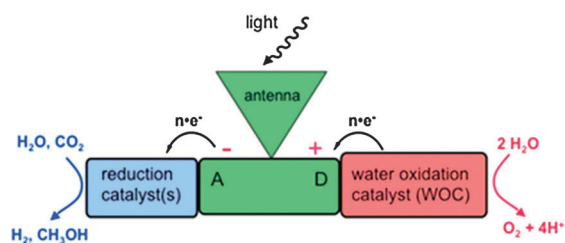
### 1b. The catalytic water oxidation problem in green fuel production

The sustained production of fuels from renewable resources requires multiple unit operations and entails many engineering demands. We focus on one subset of this, the production of solar fuels, in part because this is the area of greatest intellectual ferment and effort in academe and since sunlight must ultimately be used as the power source.<sup>23</sup> The two prominent foci of the solar fuel effort are hydrogen production *via* water splitting and carbon-based fuel production *via* CO<sub>2</sub> reduction (eqn (1) and (2)).



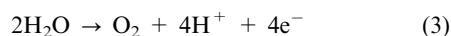
There are several light-to-chemical-energy conversion platforms that facilitate these reactions but the most prominent ones are photoelectrochemical or photoelectrosynthesis cells, including the dual semiconductor nanowire arrays separated by an ion conducting membrane,<sup>4</sup> and various electron donor–acceptor (EDA) systems interfaced with catalysts (Fig. 1).<sup>24–33</sup> At present, it is not clear which platform(s) will ultimately be triumphant. As for energy use itself (every type of energy will be needed to address the gargantuan global demand in the near future), it is likely that there will be multiple solar fuel generating structures and/or devices ultimately. Each platform has evident pros and cons, and which proceeds to full development and commercialization will likely be dictated not only by overcoming some technical hurdles but also by tackling processing, production and other commercialization challenges.

All solar fuel generating platforms (nanostructures, devices, *etc.*) must perform four linked operations efficiently: (1) absorb light with charge separation; (2) capture of the resulting charge-separated state (exciton) by removal of either the electron or the hole; (3) transfer multiple electrons to a catalyst that reduces water or carbon dioxide; and (4) transfer multiple holes on the opposite end of the nanostructure or device to a water oxidation catalyst (WOC) that evolves oxygen, *i.e.* catalyzes water oxidation, eqn (3). There is considerable ongoing research targeting each unit operation. Advances are being made in each at a rapid pace. Photosensitizer and reduction catalyst chemistry is more



**Fig. 1** General solar fuel scheme for electron-donor–acceptor + catalysts. The charge-separated excited state of the EDA unit is captured by electron transfer to the reduction catalyst side (left) and/or by hole transfer to the water oxidation catalyst (right). The net reaction is conversion of light energy and H<sub>2</sub>O and/or CO<sub>2</sub> (top and left) to fuels and O<sub>2</sub> (bottom).

researched and developed than water oxidation catalyst chemistry but insightful findings are occurring in all areas. Integration of these units (Fig. 1) for optimal turnover (solar fuel production) and understanding and optimizing the interfaces between these operating units are leading critical goals at present.



Water must be the ultimate source of electrons and protons in solar fuel generation. No other reducing agent has the capacity, ultimately, to meet the projected demand for fuel energy on a global scale while producing no waste. Thus working within the confines of two realizations is prudent: that sunlight and water sooner or later must be employed as the energy and electron + proton sources to produce a good percentage of the fuel in the future. Eqn (1) and (2), Fig. 1, and much past and ongoing research establish this point. This clearly delineates the central importance of WOCs in green fuel production.<sup>26,34–37</sup> Whether one is using light energy (again, ultimately unavoidable) or electric energy (applied potentials on anodes interfaced with the catalyst), better WOCs must be realized.

### 1c. General catalysis issues relating to water oxidation

A range of homogeneous<sup>38–55</sup> and heterogeneous<sup>29,56–69</sup> WOCs, including some immobilized homogeneous catalysts<sup>31,70–72</sup> have been discovered or developed. Intense research continues on both types at present. Heterogeneous catalysts of all kinds, including WOCs, tend to be more robust, more easily prepared in quantity and less expensive than their homogeneous counterparts. However, they are typically slower per active site and less selective than homogeneous catalysts. Homogeneous catalysts not only exhibit higher rates and selectivities, but also are far easier to study. This ease of quantitative investigation for soluble catalysts includes elucidation of their geometric and electronic structures as well as their mechanism(s) of action. Such detailed molecular-level information leads to more rational optimization of turnover rates, interface chemistry with light absorbers (photosensitizers, *etc.*) and stability. In short, both heterogeneous and homogeneous catalysts have major advantages and each type has major disadvantages. Our approach to the catalytic water oxidation problem was and is to use oxidatively, hydrolytically and thermally stable POMs as multi-dentate ligands for soluble WOCs (general properties of POMs and information on POM WOCs are discussed below).

Determining whether a particular catalyst and catalytic process operates under homogeneous and heterogeneous conditions has been an issue of intellectual interest for more than 30 years.<sup>73</sup> In other words, is the well-defined, soluble, molecular compound one adds at the beginning of the catalytic reaction the true catalyst or is it a precursor for particles that are the true catalyst? There are several well documented pitfalls in this area including the fact that metal or metal oxide particles resulting from decomposition of the initial compound can exist, in some instances for times longer than the catalytic process itself, as nanoparticles that are not readily detected by many techniques. In the 1970s and 1980s, the main focus was whether homogeneous organometallic catalysts for several processes under reductive conditions (alkene hydrogenation, some polymerizations, others) involved the organometallic complex itself or metal particles derived from reductive decomposition of this complex. More recently the same conundrum has arisen for oxidation systems, including POMs, *i.e.* are the POM units or metal oxide nanoparticles (or films) derived from hydrolytic POM decomposition, the actual catalyst.

Three types of stability are relevant for catalysts and thus for the catalysts in solar fuel generating structures, namely oxidative, hydrolytic and thermal. The first two are critical and represent challenges in the design of all units, and in particular the WOC. Thermal stability is less critical in part because most solar fuel generation technologies (prominently, photoelectrochemical cells, EDA + catalyst systems, and PV units interfaced with electrolyzers) will not usually be required to operate at elevated temperatures. However, oxidative and hydrolytic stability are both critical because the WOC must react with and doubtless in most cases be immersed in water, and it will produce oxygen. The challenges are that all the molecular, homogeneous WOCs, with the exception of the POM systems, have organic ligands that are thermodynamically unstable in the presence of O<sub>2</sub>/air with respect to CO<sub>2</sub> and H<sub>2</sub>O. Indeed all known catalysts with such ligands ultimately succumb to inactivation by ligand oxidation. Death typically comes to all such WOCs at turnover numbers (TON) that are orders of magnitude lower than those assessed as necessary (*ca.* 10<sup>9</sup>; see below). Nearly all these coordination compound WOCs are also susceptible to hydrolysis although there are few inactivation studies of these catalysts by hydrolysis because oxidative degradation is far faster than hydrolytic degradation. Again, POM systems are distinct and attractive in this context because they are carbon-free and thus oxidatively resistant while also being hydrolytically stable in certain pH ranges. The pH range of thermodynamic stability with respect to hydrolysis and metal oxide formation depends on the type of POM and its metal composition, among other factors. These factors are controllable.

The practically important issue for all catalysts and catalytic processes, including WOCs and other multi-electron-transfer catalysts relevant to solar fuel production, is not whether they are functioning homogeneously or heterogeneously, but whether they are fast, selective and stable, the 3 general paradigms that underlie all catalytic science and technology.<sup>74–76</sup> Nonetheless, sorting out what is going on in a catalytic reaction at the molecular level does have some practical aspects. Knowing everything about the catalytic active site under turnover conditions

facilitates optimization of catalytic operation under useful conditions (enables delineation of engineering parameters, *etc.*). Some points of general focus regarding catalysts include (a) the electronic and steric attributes of the catalyst active site, (b) the phase location of active specie(s), *i.e.* is it soluble, insoluble or both (sometimes solid-solution equilibria exist between catalytically competent structures in both phases), and (c) are other species in the system involved; for example, are co-catalysts operating.

A final consideration in catalysis and one highly pertinent to the catalysis of multi-electron transfer events is that the reaction rates depend greatly on the extra driving force present in the system. Clearly, from Marcus theory and other models of reactivity, reaction rates increase with driving force, at least in regular (Marcus non-inverted) region. It is frequently straightforward experimentally to increase the thermodynamic driving force for a catalyzed process, and many investigators do this yet they are not sensitive to, nor do they acknowledge the fact that this will obscure determination of how effective the catalyst actually is. For electrocatalytic or photoelectrocatalytic processes, for example, one simply needs to increase the external bias (potential) on the working electrode; for chemical reactions, one can use a more potent reagent (oxidant or reductant). At some point increasing the additional driving force will overcome the activation energy of the rate-limiting step and reaction will proceed. For electrochemical processes, this additional driving force is termed the overpotential. In short, nearly all reactions will take place if sufficient additional thermodynamic driving force is applied. *Catalysis is most important and most relevant when the rate accelerations are seen under conditions with little or no externally applied driving force.* We need WOCs and other multi-electron-transfer catalysts that are truly effective at minimal overpotentials. A final corollary of this reality is that it is rarely meaningful to compare catalytic processes (rates, selectivities) when the conditions in the different reactions are not similar, particularly if one reaction is being “helped” by application of an external driving force and another is not.

#### 1d. Requirements of a viable water oxidation catalyst (WOC)

The ensemble of challenges that a useful WOC must exhibit are beyond those of most conventional homogeneous catalysts.

First, the catalyst must be able to accumulate four oxidizing equivalents and to do so with redox levelling. Most redox processes in organic synthesis and biology are two-electron processes and there are many single electron events as well. Processes involving more than two electrons are rare, but among the outliers are photosynthetic water oxidation (eqn (3)) catalyzed by the oxygen evolving center (OEC) in Photosystem II, a four-electron process,<sup>35,77–82</sup> and nitrogen fixation (reduction) to ammonia, a six-electron process.<sup>83–85</sup> Redox levelling is the popular term given to multi-electron processes that proceed over a narrow potential range. In other words, the initial and successive redox events, all of which are needed for the net transformation, take place at closely spaced potentials (*i.e.* energies). Redox levelling is facilitated most prominently in systems that involve coupling of proton transfer events and electron transfer events. Using the four-electron oxidation of

water by the OEC as a classical example, as each successive electron is removed from this  $\text{Mn}_4\text{CaO}_4$  catalytic core, a proton is also removed to counteract the increased charge induced by the oxidation (electron transfer) event. The charge neutralization keeps the energy low. In general, the overall charge on a redox active structure (molecule, POM, nanoparticle, *etc.*) is a major determinant of the ground and excited state potentials of that structure,<sup>86</sup> and without proton-coupled electron transfer (PCET) or some other mechanism to neutralize accumulating charge, the energies for the subsequent electron transfer events increase dramatically and frequently nonlinearly. This would largely preclude energetically facile catalysis of most multi-electron transfer events. The central importance of PCET in multi-electron transfer processes, and in particular the catalysis of such reactions, has been one factor in the popularity of this topic in recent years. There have been numerous recent experimental<sup>87–95</sup> and theoretical<sup>96–100</sup> studies on PCET, and this phenomenon has been addressed in some POM studies.<sup>101</sup>

A second requirement of a viable WOC is that of stability. Projections from engineers, corporate technology managers and others are that a commercially viable solar fuel generating nanostructure or device must last for at least  $10^8$  turnovers and in some instances probably over  $10^9$  turnovers. Thus all the components in these devices must also last that long. This immediately defines a major challenge to the catalytic scientist because no known catalyst, either biological or abiological (synthetic), is this stable. Even the most robust biological catalysts are orders of magnitude less stable than this, and for a good reason: it is neither energetically outrageous nor entropically prohibitive for biological catalysts (enzymes, ribozymes, *etc.*) to be broken down and re-constituted metabolically. Efficient self-repair mechanisms, including DNA-encoded (enzymatic) ones are extant for most macromolecular biological catalysts.<sup>102,103</sup> In contrast, there is generally no repair possible in synthetic catalytic systems except in the rare cases where the active form of the catalyst is also thermodynamically stable under turnover conditions. Self-adjusting and self repairing POMs<sup>104–106</sup> and metal oxide catalysts<sup>58,107,108</sup> are well established and these properties stem from having catalysts that are dynamic (components can equilibrate under catalytic conditions) and the active form is in a thermodynamic minimum. POMs are the best general molecular example where such conditions are operable.

A third requirement of a viable WOC is that it must be, like all catalysts, fast and selective. A fourth requirement in context with solar fuel generation devices is that the WOC must be amenable to interfacing with the photosensitizer unit(s) without sacrificing any of the other essential attributes noted above. A fifth requirement, one of practicality given the projected costs and the potential global scale of solar fuel production, is that the WOC, as well as other components of the device must be inexpensive to make in bulk. This in turn demands that the WOC and other components be devoid of rare and expensive elements. Additional points are that WOCs like the other components in a solar fuel device (*e.g.* Fig. 1) need to be amenable to detailed study and examination so that their properties can be matched to the other device components.

Given that four oxidizing equivalents must be stored in a WOC (active or proximal structure) to affect water oxidation,



a systematic evaluation of many compounds was undertaken by several groups to see if complexes with only one redox active metal could catalyze water oxidation. It is quite reasonable from multiple vantages that eqn (3) could also be facilitated by two doubly-oxidized species undergoing a bimolecular reaction to form the oxygen–oxygen single bond in  $O_2$ .<sup>109</sup> There are now several examples of single-site WOCs.<sup>47,52,53,109–113</sup> Single-site POM-based WOCs were reported by the groups of Fukuzumi,<sup>49</sup> and Sakai.<sup>114</sup>

### 1e. General properties of polyoxometalates (POMs)

POMs are early transition metal oxygen anion clusters that spontaneously form in water when either soluble, molecular monomeric transition metal precursors such as  $[WO_4]^{2-}$  or insoluble metal hydroxides or oxides such as  $WO_3$  hydrate or  $V_2O_5$  are adjusted to the appropriate pH.<sup>115–125</sup> The most abundant POMs are based on W(vi), Mo(vi), V(v), V(vi), Nb(v) or Ta(v) in that order. There are thousands of polyoxotungstates (polytungstates) and almost no polytantalates. The fundamental acid–base and hydrolytic properties of these POM-forming elements dictate that polytungstates, polymolybdates and polyvanadates form in and are compatible with lower pH values, while the polyniobates and polytantalates form in and are compatible with higher pH values.<sup>126,127</sup> Mixing these elements in an appropriate synthesis, for example, to prepare polytungstoniobates (alternatively “polyniobotungstates”) makes the resulting POM hydrolytically stable in intermediate pH values. Most POMs contain one or more heteroatoms (typically p or d block elements found in one or more positions internal to the polyanion unit). These “heteropolyanions” or “heteropoly compounds” tend to be stable hydrolytically over wider pH ranges than the isopolyanions which contain only the metal and oxygen atoms as exemplified by  $[W_{10}O_{32}]^{4-}$ ,  $[Mo_7O_{24}]^{6-}$ , and  $[V_{10}O_{28}]^{6-}$ .<sup>125</sup> In the common Keggin structure,  $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ , the central heteroatom,  $X^{n+}$ , can be most of the elements in the periodic table, and 1, 2 or 3 of the original tungsten atoms (usually a terminal  $[W=O]^{4+}$  unit) can be removed and replaced with other p or d block elements including those with appended organic groups.<sup>128–130</sup> Thus the thousands of polytungstates made to date barely<sup>131</sup> scratch the surface of the structures that are, in principal, possible and synthetically accessible. More complex POMs, particularly the giant polymolybdates pioneered by Achim Müller,<sup>132–148</sup> as many of the polytungstates, are prepared in one-pot condensation reactions at the right pH and ionic strength. However, many POMs in recent years are made by multi-step reactions as in conventional, serial organic synthesis. One example of the latter approach is a multi-step synthesis of Keggin tungstoaluminates.<sup>149</sup>

POMs have applications or potential applications in several areas including medicine,<sup>150–163</sup> magnetism,<sup>147,164–167</sup> high performance materials, chirality,<sup>168–177</sup> and others.<sup>178</sup> However, the dominant use of POMs is in catalysis.<sup>104,179–193</sup> Several processes have been commercialized where the POM serves either as an acid catalyst (usually a superacid) or an oxidation catalyst. In recent years, a host of organic POM derivatives have been made,<sup>130,194–200</sup> and some of these may be of value in the construction of solar fuel production assemblies or devices.

The great majority of POMs bear high negative charges and thus have a commensurate number of counter-cations. Ion pairing in POM systems varies widely with the POM properties, particularly polyanion unit charge, and when operable, controls not only POM synthesis (self assembly and equilibration processes),<sup>115,117,118,125,201</sup> but also the redox potentials, reactivities and other properties of the polyanion moiety.<sup>86,202–210</sup> The chemistry of polyperoxometalates, that form from and can be in equilibrium with POMs,<sup>211–214</sup> is also strongly influenced by counterions and ion pairing.<sup>215</sup> Ion pairing is without doubt significant in POM-ionic liquid systems currently under investigation by Bond, Wedd and their co-workers,<sup>55</sup> and underlies innovative materials self assembly chemistry being developed by Cronin and co-workers.<sup>216–219</sup> While ion pairing is well documented in POM systems, one aspect of it is little studied to date, namely the role of pairing in the catalysis of redox reactions, and in particularly multi-electron redox reactions like water oxidation. A phenomenon analogous to PCET usually takes place during POM-catalyzed redox processes, namely the pairing of counter-cations with their respective polyanions occurs and the degree of this electrostatic association depends on the number of electrons removed or added to the polyanion.

### 2a. Overview of polyoxometalate water oxidation catalysts (POM WOCs)

Table 1 summarizes the salient features of the POM WOC publications to date. All the POM WOCs characterized by X-ray crystallography are shown in Fig. 2. While the stability of POM WOCs is addressed separately in Section 2c, many experiments by several groups on this topic are noted in this section.

In 2004, Shannon and co-workers reported the electrochemical production of oxygen using pulsed voltammetry in 0.1 M sodium phosphate buffer (pH 8.0) solution in the presence of a transition-metal-substituted POM,  $Na_{14}[Ru^{III}_2Zn_2(H_2O)_2(ZnW_9O_{34})_2]$  (**Ru<sub>2</sub>ZnPOM**).<sup>220</sup> A catalytic current corresponding to oxygen production was observed when the working electrode potential was stepped repeatedly to a positive value. The calculated  $E_{1/2}$  (~0.750 V) for electrocatalytic oxygen evolution approaches the thermodynamic value (~0.760 V vs. NHE) for water oxidation. They showed that mono-ruthenium complex,  $[Ru^{III}(H_2O)PW_9O_{39}]^{4-}$  was inactive for water oxidation under the same conditions. The X-ray crystal structure of **Ru<sub>2</sub>ZnPOM** (Fig. 2(a)) shows W–Ru disorder in the two belt positions, and other challenges.

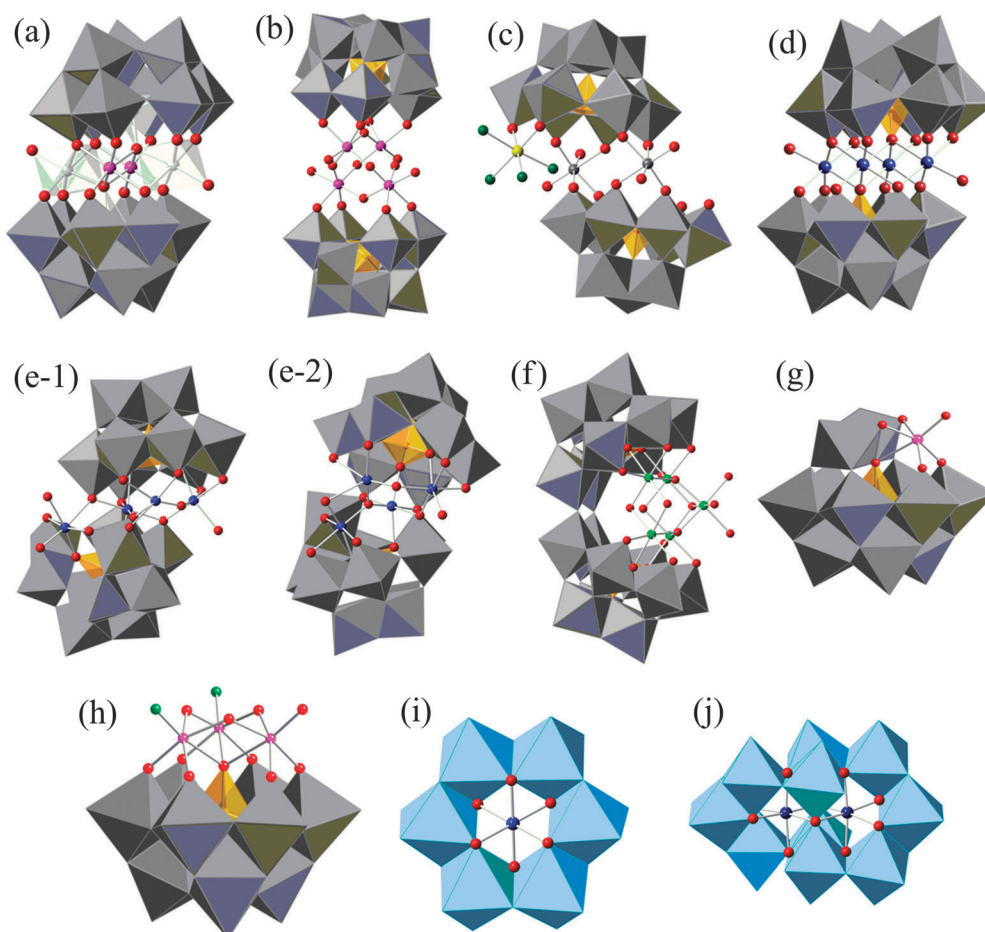
The major breakthrough in POM WOC development was achieved in 2008, when two groups simultaneously reported the synthesis (by different routes), solid state and solution characterization, and homogeneous catalytic water oxidation activity of the tetra-ruthenium polytungstate,  $[Ru_4(\mu-O)_4(\mu-OH)_2(H_2O)_4(\gamma-SiW_{10}O_{36})_2]^{10-}$  (**Ru<sub>4</sub>SiPOM**). Fig. 2(b) shows the X-ray crystal structure of **Ru<sub>4</sub>SiPOM**.<sup>221,222</sup> The Hill group evaluated oxygen evolution at pH 7.2, in 20 mM phosphate buffer and used  $[Ru(bpy)_3]^{3+}$  as the oxidant. Under these conditions, a turnover number (TON) of ~18, corresponding to a turnover frequency (TOF) of 0.45–0.6 s<sup>-1</sup>, was obtained. The Bonchio group assessed oxygen evolution at pH ~0.6 using excess Ce(IV) as the oxidant and reported a

**Table 1** Summary of published POM WOCs to date

Entry #	POM catalyst	Representative reaction conditions	Turnover frequency (TOF)	POM structures	Ref. (year)
1	Na <sub>14</sub> [Ru <sup>III</sup> <sub>2</sub> Zn <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (ZnW <sub>9</sub> O <sub>34</sub> ) <sub>2</sub> ]	Electrochemical water oxidation using pulsed voltammetry in 0.1 M sodium phosphate buffer (pH 8.0) with 2 μM catalyst	No data	Fig. 2(a)	<sup>220</sup> (2004)
2	Rb <sub>8</sub> K <sub>2</sub> [{Ru <sub>4</sub> O <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> }-( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	[Ru(bpy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> as the oxidant, 20 mM sodium phosphate buffer (pH 7.2)	0.45–0.60 s <sup>-1</sup>	Fig. 2(b)	<sup>221</sup> (2008)
3	Rb <sub>8</sub> K <sub>2</sub> [{Ru <sub>4</sub> O <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> }-( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	Xe lamp, 420–520 nm, 1.0 mM [Ru(bpy) <sub>3</sub> ] <sup>2+</sup> , 5.0 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 5.0 μM catalyst, 20 mM sodium phosphate buffer (pH 7.2)	8 × 10 <sup>-2</sup> s <sup>-1</sup>	Fig. 2(b)	<sup>223</sup> (2009)
4	Rb <sub>8</sub> K <sub>2</sub> [{Ru <sub>4</sub> O <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> }-( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	1.15 mM [Ru(bpy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> as the oxidant, 20 mM sodium phosphate buffer (pH 7.2)	No data	Fig. 2(b)	<sup>224</sup> (2009)
5	Rb <sub>8</sub> K <sub>2</sub> [{Ru <sub>4</sub> O <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> }-( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	All calculations were performed using the Gaussian 03 program	N/A	Fig. 2(b)	<sup>225</sup> (2009)
6	Rb <sub>8</sub> K <sub>2</sub> [{Ru <sub>4</sub> O <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> }-( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	All reported calculations were performed using the TURBOMOLE software, version 5.10	N/A	Fig. 2(b)	<sup>226</sup> (2010)
7	Cs <sub>9</sub> [( $\gamma$ -PW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> Ru <sup>IV</sup> <sub>4</sub> O <sub>5</sub> (OH)(OH <sub>2</sub> ) <sub>4</sub> ]	Xe lamp (420–520 nm), 5.1 μM catalyst, 1.0 mM [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> , 5 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 20 mM Na <sub>2</sub> SiF <sub>6</sub> buffer (pH 5.8)	TOF <sub>initial</sub> = 0.13 s <sup>-1</sup>	Fig. 2(b)	<sup>235</sup> (2010)
8	K <sub>14</sub> [(IrCl <sub>4</sub> )KP <sub>2</sub> W <sub>20</sub> O <sub>72</sub> ]	1.4 mM [Ru(bpy) <sub>3</sub> ] <sup>3+</sup> , 20 μM catalyst, 20 mM sodium phosphate buffer (pH 7.2)	No data	Fig. 2(c)	<sup>238</sup> (2009)
9	Na <sub>10</sub> [Co <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ( $\alpha$ -PW <sub>9</sub> O <sub>34</sub> ) <sub>2</sub> ]	1.5 mM [Ru(bpy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> as oxidant, 30 mM NaPi buffer (pH 8.0)	> 5 s <sup>-1</sup>	Fig. 2(d)	<sup>239</sup> (2010)
10	Na <sub>10</sub> [Co <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ( $\alpha$ -PW <sub>9</sub> O <sub>34</sub> ) <sub>2</sub> ]	Xe lamp (420–470 nm), 1.0 mM [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> , 5.0 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 80 mM sodium borate buffer (pH 8.0)	No data	Fig. 2(d)	<sup>240</sup> (2011)
11	K <sub>10.2</sub> Na <sub>0.8</sub> [{Co <sub>4</sub> ( $\mu$ -OH)(H <sub>2</sub> O) <sub>3</sub> }(Si <sub>2</sub> W <sub>19</sub> O <sub>70</sub> )]	Xe lamp (420–520 nm), 10 μM catalyst, 1.0 mM [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> , 5 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 25 mM sodium borate buffer (pH 9.0)	0.1 s <sup>-1</sup>	Fig. 2(e-1) and (e-2)	<sup>241</sup> (2012)
12	K <sub>10</sub> H <sub>2</sub> [Ni <sub>5</sub> (OH) <sub>6</sub> (OH <sub>2</sub> ) <sub>3</sub> (Si <sub>2</sub> W <sub>18</sub> O <sub>66</sub> )]	LED lamp, 455 nm, 1.0 mM [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> , 5 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 80 mM sodium borate buffer (pH 8.0)	No data	Fig. 2(f)	<sup>242</sup> (2012)
13	Cs <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]/Li <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	4.3 mM catalyst, 0.172 M (NH <sub>4</sub> ) <sub>2</sub> [Ce <sup>IV</sup> (NO <sub>3</sub> ) <sub>6</sub> ], in H <sub>2</sub> O (pH 0.6)	TOF <sub>max</sub> > 0.125 s <sup>-1</sup>	Fig. 2(b)	<sup>222</sup> (2008)
14	Li <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	1 mM catalyst in H <sub>2</sub> O (pH 0.6)	N/A	Fig. 2(b)	<sup>227</sup> (2009)
15	Li <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]@Dendron-MWCNT	ITO deposited with catalyst as working electrode, aqueous PBS buffer solution (pH 7.0), scan rate: 20 mV s <sup>-1</sup> in the range of 0–1.6 V, reference electrode: Ag/AgCl (3 M KCl), counter electrode: platinum wire, T = 298 K	From 0.01 s <sup>-1</sup> ~ 0.085 s <sup>-1</sup> @ overpotential from 0.35 V to 0.6 V	Fig. 2(b)	<sup>228</sup> (2010)
16	Li <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]@Dendron-MWCNT	ITO deposited with catalyst as working electrode, aqueous PBS buffer solution (pH 7.0), scan rate: 20 mV s <sup>-1</sup> in the range of 0–1.6 V, reference electrode: Ag/AgCl (3 M KCl), counter electrode: platinum wire, T = 298 K	from 0.01 s <sup>-1</sup> to 0.085 s <sup>-1</sup> @ overpotential from 0.35 V to 0.6 V	Fig. 2(b)	<sup>229</sup> (2011)
17	Li <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]@MWCNT	A disk screen-printed carbon (DSC) electrode deposited with catalyst as working electrode, aqueous PBS buffer solution (pH 7.0), scan rate: 20 mV s <sup>-1</sup> in the range of 0–1.4 V, reference electrode: Ag/AgCl (3 M KCl), counter electrode: platinum wire, T = 298 K	No data	Fig. 2(b)	<sup>230</sup> (2011)
18	Cs <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	Surelite Continuum Surelite II Nd:YAG laser (excitation at 355 nm and 532 nm, half-width 8 ns), 47.6 μM [Ru(bpy) <sub>3</sub> ] <sup>2+</sup> , 5.0 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , varying [cat.], 10 mM phosphate buffer (pH 7.0) or TiO <sub>2</sub> film sensitized with [Ru(bpy) <sub>2</sub> (dpp)] <sup>2+</sup>	N/A	Fig. 2(b)	<sup>231</sup> (2010)
19	Cs <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	50 W halogen lamp ( $\lambda$ > 550 nm), 60 μM catalyst, 0.1 mM [Ru{(dpp)Ru(bpy) <sub>2</sub> }] <sub>3</sub> (PF <sub>6</sub> ) <sub>8</sub> , 10 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> and 50 mM Na <sub>2</sub> SO <sub>4</sub> , 10 mM KH <sub>2</sub> PO <sub>4</sub> buffer (pH 7.2)	TOF = 8 × 10 <sup>-3</sup> s <sup>-1</sup> @ 60 μM catalyst	Fig. 2(b)	<sup>233</sup> (2010)
20	Cs <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	33 mM H <sub>2</sub> O <sub>2</sub> as the shunt oxidant, varying [cat.], 50 mM phosphate buffer (pH 7.0)	TOF > 1.27 s <sup>-1</sup> @ 29.2 μM catalyst	Fig. 2(b)	<sup>234</sup> (2011)
21	Cs <sub>10</sub> [Ru <sub>4</sub> ( $\mu$ -O) <sub>4</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> -( $\gamma$ -SiW <sub>10</sub> O <sub>36</sub> ) <sub>2</sub> ]	Surelite Continuum Surelite II Nd:YAG laser (excitation at 355 nm and 532 nm, half-width 6–8 ns), 0.1 mM [Ru(bpy) <sub>3</sub> ] <sup>2+</sup> , 5.0 mM Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , varying [cat.], 80 mM phosphate buffer (pH 7.0)	TOF = 280 s <sup>-1</sup> @ 0.5 μM catalyst	Fig. 2(b)	<sup>232</sup> (2012)
22	Cs <sub>5</sub> [Ru <sup>III</sup> (H <sub>2</sub> O)SiW <sub>11</sub> O <sub>39</sub> ]	0.3 mM catalyst, 6 mM (NH <sub>4</sub> ) <sub>2</sub> [Ce <sup>IV</sup> (NO <sub>3</sub> ) <sub>6</sub> ] in 0.1 M HNO <sub>3</sub>	No data	Fig. 2(g)	<sup>49</sup> (2011)

Table 1 (continued)

Entry #	POM catalyst	Representative reaction conditions	Turnover frequency (TOF)	POM structures	Ref. (year)
23	$\text{Cs}_3[\text{Ru}^{\text{III}}(\text{H}_2\text{O})\text{GeW}_{11}\text{O}_{39}]$	0.3 mM catalyst, 6 mM $(\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]$ in 0.1 M $\text{HNO}_3$	No data	Fig. 2(g)	<sup>49</sup> (2011)
24	$\alpha\text{-K}_6\text{Na}[\{\text{Ru}_3\text{O}_3(\text{H}_2\text{O})\text{Cl}_2\}(\text{SiW}_9\text{O}_{34})]$	LED lamp (470 nm), 50 $\mu\text{M}$ catalyst, 1 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 5 mM $\text{Na}_2\text{S}_2\text{O}_8$ , 20 mM $\text{Na}_2\text{SiF}_6$ buffer (pH 5.8)	$\text{TOF}_{\text{initial}} = 0.7 \text{ s}^{-1}$	Fig. 2(h)	<sup>243</sup> (2012)
25	$\text{K}_{11}\text{Na}_1[\text{Co}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2]$	LED lamp (470 nm), 42 $\mu\text{M}$ catalyst, 1 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 5 mM $\text{Na}_2\text{S}_2\text{O}_8$ , 20 mM $\text{Na}_2\text{SiF}_6$ buffer (pH 5.8)	$\text{TOF}_{\text{initial}} = 0.4 \text{ s}^{-1}$	Fig. 2(d)	<sup>243</sup> (2012)
26	$(\text{NH}_4)_3[\text{CoMo}_6\text{O}_{24}\text{H}_6] \cdot 7\text{H}_2\text{O}$	300 W Xe lamp (400–490/800 nm), 20 $\mu\text{M}$ catalyst, 0.4 mM $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$ , 3 mM $\text{Na}_2\text{S}_2\text{O}_8$ , 0.1 M borate buffer solution (pH 8.0)	$\text{TOF}_{\text{initial}} = 0.11 \text{ s}^{-1}$	Fig. 2(i)	<sup>114</sup> (2012)
27	$(\text{NH}_4)_6[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4] \cdot 7\text{H}_2\text{O}$	300 W Xe lamp (400–490/800 nm), 10 $\mu\text{M}$ catalyst, 0.4 mM $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$ , 3 mM $\text{Na}_2\text{S}_2\text{O}_8$ , 0.1 M borate buffer solution (pH 8.0)	$\text{TOF}_{\text{initial}} = 0.16 \text{ s}^{-1}$	Fig. 2(j)	<sup>114</sup> (2012)
28	$\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]/\text{MCN}$	ITO deposited with catalyst as working electrode, 0.1 M phosphate buffer solution at pH 7, scan rate $20 \text{ mV s}^{-1}$ in the range of 0–1.5 V. All the potentials were referred to the $\text{Ag}/\text{AgCl}$ (3 M KCl) electrode	$\sim 0.3 \text{ s}^{-1}$	Fig. 2(d)	<sup>70</sup> (2012)



**Fig. 2** X-ray crystal structure of polyoxometalates in combined ball-and-stick and polyhedral representations corresponding to Table 1. Red: O; magenta: Ru; blue: Co; green: Ni; yellow: Ir; dark teal: Cl; orange polyhedra:  $\text{PO}_4/\text{SiO}_4/\text{GeO}_4$ ; white polyhedra:  $\text{ZnO}_4/\text{ZnO}_6$ ; grey polyhedra:  $\text{WO}_6$ ; light blue polyhedra:  $\text{MoO}_6$ .

TON of 500 with an initial TOF of  $0.125 \text{ s}^{-1}$ . Subsequently **Ru<sub>4</sub>SiPOM** was shown to catalyze water oxidation with visible light using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a photosensitizer and  $\text{S}_2\text{O}_8^{2-}$  as a sacrificial electron acceptor.<sup>223</sup> Under turnover conditions

(Table 1, entry 3), up to 350 turnovers were obtained with an initial TOF and quantum yield ( $\Phi(\text{O}_2)$ ) of  $0.08 \text{ s}^{-1}$  and 9%, respectively. Reuse of the isolated catalyst from post-reaction solution (precipitated using  $[\text{Ru}(\text{bpy})_3]^{2+}$ ) results in continuous

catalytic water oxidation in the initial run. The mechanism of water oxidation by using  $[\text{Ru}(\text{bpy})_3]^{3+}$  or  $\text{Ce}(\text{IV})$  oxidants has also been studied in depth.<sup>224–227</sup> **Ru<sub>4</sub>SiPOM** undergoes sequential oxidation from  $\text{Ru}(\text{IV})_4$  resting state to the  $\text{Ru}(\text{V})_4$  state.<sup>224–227</sup> There was no evidence of hydrolytic decomposition of the **Ru<sub>4</sub>SiPOM** WOC into the metal oxides ( $\text{RuO}_2$ ,  $\text{WO}_3$ ) under either thermal or photo-driven water oxidation conditions in many experiments conducted by both the Hill and Bonchio groups.

Subsequently, Bonchio's group constructed nanostructured oxygen evolving anodes comprising an assembly of **Ru<sub>4</sub>SiPOM** electrostatically associated with polyamidoamine (PAMAM) dendrimers bound to conductive multiwalled carbon nanotubes (MWCNTs) scaffolds on ITO electrodes.<sup>228,229</sup> These nano-assembly anodes exhibit good mechanical properties, high surface area, good thermal stability, and under optimal conditions, perform efficient water oxidation with TOF values of  $0.01 \text{ s}^{-1}$  and  $0.085 \text{ s}^{-1}$  at overpotentials of 0.35 V and 0.6 V, respectively. Although this work addressed the successful design of water-splitting electrodes with good efficiency, operating voltage and current density, the authors did not evaluate the long-term durability and the retention of electrocatalytic properties of these multi-component nano-assembly anodes. By following the similar strategy, a microwave-assisted, solvent-free synthetic (amine addition) approach was developed to directly functionalize the MWCNT surface with positive charges.<sup>230</sup> The resulting functionalized CNTs scaffolds were used to assemble functional hybrid nanocomposites (**Ru<sub>4</sub>SiPOM@MWCNTs**) by electrostatically scavenging negatively-charged **Ru<sub>4</sub>SiPOM** WOCs. The electrocatalytic activity of these hybrid nanocomposites was evaluated on the surface on ITO and disk screen-printed carbon (DSC) electrodes. Under the experimental conditions listed in Table 1, the **Ru<sub>4</sub>SiPOM@MWCNT@DSC** electrode showed enhanced electrocatalytic water oxidation activity relative to the ITO analogue. This was ascribed to the improved stability and reduced ohmic losses associated with the DSC electrode. Again, the long-term stability and structural integrity of these nano-structured hybrid materials were not investigated.

The oxidation (hole scavenging process) of **Ru<sub>4</sub>SiPOM** by photogenerated  $\text{Ru}^{\text{III}}$  oxidants was investigated both in homogeneous solution and on a sensitized  $\text{TiO}_2$  semiconductor surface. The solution rate constant of  $2.1 \pm 0.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was noted.<sup>231</sup> Under both experimental conditions (Table 1, entry 18), the highly negative POM catalyst electrostatically interacts with the positively charged oxidants. Simultaneously, the large rigid POM ligands stabilize the redox active  $\text{Ru}_4$  core, lowering the reorganization energy for the observed redox process. The fast hole filling rates suggest the possibility of using this new catalyst, **Ru<sub>4</sub>SiPOM**, in practical photochemical water splitting devices. Natali and co-workers conducted a similar but more detailed study that confirmed the formation of a 1 : 4 stoichiometric ratio ion pair between the highly anionic **Ru<sub>4</sub>SiPOM** catalyst and the cationic  $[\text{Ru}(\text{bpy})_3]^{2+}$  sensitizer using both static luminescence quenching of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited state and flash photolysis experiments.<sup>232</sup> The rate of the hole scavenging from  $[\text{Ru}(\text{bpy})_3]^{3+}$  generated *in situ* by **Ru<sub>4</sub>SiPOM** is remarkably high ( $3.6 \pm 0.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and similar to the value obtained in a previous study.<sup>231</sup> The flash photolysis experiments show that, under optimal experimental conditions (shown in Table 1), a single molecule of **Ru<sub>4</sub>SiPOM**

can catalyze the reduction of *ca.* 45 equivalents of  $[\text{Ru}(\text{bpy})_3]^{3+}$  in 40 ms, corresponding to an average TOF of  $280 \text{ s}^{-1}$  for oxygen evolution. However, this very high TOF value was calculated assuming one oxygen molecule is released after four hole-scavenging events instead of using the actual oxygen yields generated during experiments. Thus, one should treat this very high TOF as a theoretical value, and not compare it to those from other experiments involving with **Ru<sub>4</sub>SiPOM**, or other POM WOCs. Conclusions from such comparisons could be misleading; they oversimplify these complicated multi-parameter catalytic multi-electron redox processes.

A photo-driven water oxidation study was also performed using a tetranuclear  $\text{Ru}(\text{II})$  dendrimer photosensitizer,  $[\text{Ru}\{\mu\text{-dpp}\}(\text{bpy})_2]_3(\text{PF}_6)_8$ , ( $\text{bpy}$  = 2,20-bipyridine;  $\text{dpp}$  = 2,3-bis(20-pyridyl)pyrazine), at 550 nm catalyzed by **Ru<sub>4</sub>SiPOM**.<sup>233</sup> Under the experimental conditions (see Table 1), a chemical yield (persulfate conversion) of 90% was obtained, corresponding to a TOF of  $0.008 \text{ s}^{-1}$ . The quantum yield ( $\Phi(\text{O}_2)$ ) was up to 30%. The authors claimed that the significant increase of light conversion efficiency is likely due to the increased stability of this specific reaction system; however, no strong evidence was given to support this contention.

**Ru<sub>4</sub>SiPOM** was also found to function as a molecular propeller associated with catalyzing the disproportionation of  $\text{H}_2\text{O}_2$  in 50 mM phosphate buffer (pH 7.0) solution (Table 1, entry 20).<sup>234</sup> Under optimal conditions, the reaction proceeds with a maximum TOF higher than  $1.27 \text{ s}^{-1}$ . This paper advanced the possibility of exploring the design of POM-based photo-propellers to achieve the bottom-up control of chemically-induced dynamics in nano-devices and functional systems.

In order to investigate the influence of different heteroatoms in the POM ligands on the redox potentials and other properties of a POM WOC, the isostructural phosphorus analogue of **Ru<sub>4</sub>SiPOM**, namely  $[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4(\gamma\text{-PW}_{10}\text{O}_{36})_2]^{7-}$  (**Ru<sub>4</sub>PPOM**), was successfully prepared and thoroughly characterized.<sup>235</sup> Two  $\text{P}(\text{V})$  centers now replace the two  $\text{Si}(\text{IV})$  positions in **Ru<sub>4</sub>SiPOM** (the central orange  $\text{XO}_4$  tetrahedra in Fig. 2(b)), resulting in a different charge on the WOC polyanion, which in turn changes the redox potentials of the complex. **Ru<sub>4</sub>PPOM** is also an effective WOC with similar (20% less) catalytic activity in photo-driven water oxidation relative to **Ru<sub>4</sub>SiPOM** under the same conditions (Table 1, entry 7) and gives a TON for catalytic water oxidation of 120 with an initial TOF of  $0.13 \text{ s}^{-1}$ .

As noted in the Introduction (Section 1d), there are now many documented single-metal-site WOCs despite the fact that water oxidation is a four-electron process.<sup>47,52,53,109–113</sup> Fukuzumi and co-workers<sup>49</sup> have made a clear case that POMs containing only one redox-active metal in the catalyst active site are viable WOCs. They documented that mononuclear  $\text{Ru}$ -substituted Keggin-type heteropolytungstates catalyze water oxidation. Specifically 0.3 mM  $[\text{Ru}^{\text{III}}(\text{H}_2\text{O})\text{SiW}_{11}\text{O}_{39}]^{5-}$  (**RuSiPOM**) or  $[\text{Ru}^{\text{III}}(\text{H}_2\text{O})\text{GeW}_{11}\text{O}_{39}]^{5-}$  (**RuGePOM**), (structures in Fig. 2(g)) in 0.1 M  $\text{HNO}_3$  solution with 6 mM  $(\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]$  (CAN) as an oxidant produce 20 and 50 turnovers of oxygen respectively. The TON for water oxidation is far lower for these Keggin WOCs than for **Ru<sub>4</sub>SiPOM**, indicating the importance (and possible synergistic effect) of a tetraruthenium core.



Isotope-labeling experiments confirmed that the oxygen atoms derive exclusively from water. Cyclic voltammetric measurements and the Pourbaix diagrams show that CAN oxidizes the Ru centers in **RuSiPOM** and **RuGePOM** to  $\text{Ru}^{\text{V}}=\text{O}$  species. Kinetic and mechanistic studies show that the  $\text{Ru}^{\text{V}}=\text{O}$  intermediates may react with water to form  $\text{Ru}^{\text{III}}\text{-OOH}$  species then subsequent two-electron oxidation by CAN and release of oxygen. Similar pathways have been quite well supported in the case of water oxidation catalyzed by monoruthenium complexes with organic ligands.<sup>113,236</sup>

With multiple thorough demonstrations that tetra-ruthenium- and mono-ruthenium-substituted POMs are efficient WOCs and thus molecular synthetically modifiable analogues of the corresponding metal oxide,  $\text{RuO}_2$ , the Hill group proceeded to investigate several other POMs containing multi-transition-metal-oxide clusters stabilized by various multi-dentate lacunary polytungstate ligands. Since  $\text{IrO}_2$  is a well known and excellent WOC,<sup>5,29,237</sup> we prepared an Ir-containing POM,  $[(\text{IrCl}_4)\text{KP}_2\text{W}_{20}\text{O}_{72}]^{14-}$  (**IrPOM**), in which an  $\text{IrCl}_4$  unit is anchored to the  $[\text{KP}_2\text{W}_{20}\text{O}_{72}]^{13-}$  polyanion through two O atoms (structure in Fig. 2(c)). **IrPOM** was characterized by NMR and other forms of spectroscopy, elemental analysis, and X-ray crystallography, which all confirmed the presence of one Ir atom per polyanion. These techniques, combined with IR, UV-vis spectra, thermal gravimetric analysis, and electrochemistry, confirmed that **IrPOM** was pure in both solid and solution states. **IrPOM** was first evaluated as a WOC using  $[\text{Ru}(\text{bpy})_3]^{3+}$  as the stoichiometric oxidant in 20 mM sodium phosphate buffer (pH 7.2). In the presence of small amounts of catalyst, the reaction time for  $[\text{Ru}(\text{bpy})_3]^{3+}$  reduction is shortened from 30 min to less than 3 min, and an oxygen yield of ~30% was obtained under non-optimized conditions (Table 1, entry 8). Not surprisingly, **IrPOM** slowly decomposes in aqueous solution to  $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$  and  $[\text{KP}_2\text{W}_{20}\text{O}_{72}]^{13-}$ . However the rate of this hydrolytic decomposition (first-order dissociation rate constant of  $1.5 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$ ) is *ca.* two orders of magnitude slower than the rate of water oxidation catalyzed by **IrPOM**. This argues that **IrPOM** itself, and not  $\text{IrO}_2$  nanoparticles arising from **IrPOM** decomposition, is the actual catalyst. In addition, **IrPOM** catalyzes water oxidation far faster than authentic  $\text{IrO}_2$  nanoparticles under otherwise identical conditions. Although **IrPOM** constitutes a tractable molecular model of iridium supported on redox-active metal oxides, the hydrolytic instability of **IrPOM** and, to a lesser extent, the cost of iridium compelled us to investigate and develop other more promising, low-cost, and earth-abundant multi-metal-substituted POMs as multi-electron transfer catalysts.

Another significant breakthrough was successfully achieved in 2010, when a tetracobalt-substituted polytungstate,  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (**Co<sub>4</sub>PPOM**; single crystal structure in Fig. 2(d)),<sup>239</sup> was demonstrated to catalyze water oxidation in the dark using  $[\text{Ru}(\text{bpy})_3]^{3+}$  as a chemical oxidant in aqueous phosphate buffer solution at pH 8.0, producing the highest TON per active site metal of any WOC at that time: over 1000 in 3 min affording a TOF of  $5 \text{ s}^{-1}$ .<sup>239</sup> Oxygen evolution yields were found to be highly pH and buffer dependent. In assessing the stability of **Co<sub>4</sub>PPOM** the authors used seven different experiments or techniques including UV-vis, IR and <sup>31</sup>P NMR spectra, *etc.* before and after

catalytic reaction. They conducted a poisoning experiment using bipyridine, a ligand that binds any free  $\text{Co}^{2+}$  rendering it catalytically inactive. They also, isolated and reused **Co<sub>4</sub>PPOM** and assessing the voltammetric behavior of the catalyst under the simulated reaction conditions. All these experiments confirmed that **Co<sub>4</sub>PPOM** remains molecular and does not decompose under these turnover conditions. No evidence for the formation of metal oxides from the possible decomposition of **Co<sub>4</sub>PPOM** catalyst was observed. Subsequently, **Co<sub>4</sub>PPOM** was demonstrated to catalyze efficient water oxidation under photo-driven conditions using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as photosensitizer and persulfate as sacrificial electron acceptor.<sup>240</sup> Under optimal conditions, a TON of over 220 and high quantum yield of 30% were obtained in pH 8.0 borate buffer.

Stracke and Finke implied in an electrocatalytic water oxidation study using **Co<sub>4</sub>PPOM**, that this POM was simply a precursor for cobalt oxide which is the actual catalyst (WOC) under their conditions and also under those in our original paper on homogeneous catalytic water oxidation.<sup>239</sup> However, their conditions are quite different than those in our paper. There is compelling evidence in these two very thorough papers that both are correct: under our conditions **Co<sub>4</sub>PPOM** does not decompose to form metal oxide; under their quite different conditions it does.

Quite recently, **Co<sub>4</sub>PPOM** was supported on mesoporous carbon nitride (MCN) scaffold to form an oxygen-evolving anode in aqueous phosphate buffer at pH 7.0.<sup>67</sup> This **Co<sub>4</sub>PPOM**/MCN composite shows excellent electrocatalytic activity and appears to exhibit synergistic coupling between the redox features of **Co<sub>4</sub>PPOM** and the MCN scaffold (uniform nanochannels, high surface area and electrical conductivity). This composite efficiently catalyzes the formation of 12.1  $\mu\text{mol}$  oxygen on passage of 5 C of charge during electrolysis, achieving a Faradaic efficiency as high as 95%. In addition, the TOF of this **Co<sub>4</sub>PPOM**/MCN catalyst reaches around  $0.3 \text{ s}^{-1}$ , which is almost six times higher ( $\sim 0.055 \text{ s}^{-1}$ ) at 1.4 V than the **Ru<sub>4</sub>SiPOM**/MWCNs hybrid catalyst of Bonchio and collaborators,<sup>228</sup> although as noted below, comparisons of different rates by different WOC systems is problematical given the large number of variables and that actual conditions used by the different laboratories are rarely identical. The stability/durability of this POM–MCN composite catalyst was confirmed by UV-Vis and XRD techniques, no obvious change was observed before or after electrolysis over 10 000 s, suggesting this POM WOC-containing hybrid composite catalyst is quite stable. However, no long-term durability study was performed, and as the authors state, an appropriately engineered electrode device is needed to address this point. XANES (X-ray absorption near edge structure) data indicate interactions and possible bond formation between **Co<sub>4</sub>PPOM** and the MCN scaffold. The authors suggest such bonds are probably responsible for the high catalytic water oxidation activity.

To assess the effect of the heteroatom on the properties of the multi-cobalt POM WOCs, a new tetracobalt-containing polyoxometalate,  $[\{\text{Co}_4(\mu\text{-OH})(\text{H}_2\text{O})_3\}(\text{Si}_2\text{W}_{19}\text{O}_{70})]^{11-}$  (**Co<sub>4</sub>SiPOM**), which co-crystallizes as a 1 : 1 mixture of two isomers (single crystal structure shown in Fig. 2(e-1) and (e-2)) was recently achieved.<sup>241</sup> **Co<sub>4</sub>SiPOM** catalyzes photo-driven water oxidation ( $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  as photosensitizer and sacrificial

electron acceptor, respectively). Under the experimental conditions in Table 1 (entry 11), a TON of  $\sim 80$ , corresponding to an initial apparent turnover frequency ( $\text{TOF}_{\text{app}}$ )  $\sim 0.1 \text{ s}^{-1}$  is observed. In contrast to **Co<sub>4</sub>PPOM**, however, which is hydrolytically stable over a wide pH range, **Co<sub>4</sub>SiPOM** undergoes hydrolysis in de-ionized water, and three aqueous buffer solutions at three different pH values: sodium acetate (pH 4.8), phosphate (pH 7.2) and borate (pH 9.0). However, the isolated hydrolysis products are *ca.* 3 times less active catalyzing water oxidation ( $\text{TOF}_{\text{app}} \sim 0.025 \text{ s}^{-1}$ ) than freshly prepared **Co<sub>4</sub>SiPOM**, indicating that the intact initial complex could be functioning as a true WOC rather than as a precursor to metal oxide nanoparticles that are the actual catalyst.<sup>241</sup>

More recently, Patzke and co-workers<sup>243</sup> prepared two sandwich-type Co- and Ni-containing silicotungstates  $[\text{M}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2]^{12-}$  ( $\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}$ ) (**Co<sub>4</sub>SiW<sub>9</sub>POM**, **Ni<sub>4</sub>SiPOM**, Fig. 2(d)) and a new triruthenium-substituted silicotungstate,  $[\{\text{Ru}_3\text{O}_3(\text{H}_2\text{O})\text{Cl}_2\}(\text{SiW}_9\text{O}_{34})]^{7-}$  (**Ru<sub>3</sub>SiPOM**, Fig. 2(h)) using the trivalent Keggin-type polydentate polyanion,  $\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ . Unfortunately, suitable single crystals were not obtained for any of these compounds. Nonetheless, various techniques (B97D/Def2-TZVP computational analysis, electrospray ionization (ESI) mass spectroscopy, FT-IR, Raman spectroscopy and elemental analysis) provided reasonable evidence for the proposed structures. The photo-driven water oxidation activity of all three compounds was investigated using a routine photocatalytic set-up. Under their experimental conditions (Table 1, entries 24, 25) initial TOFs up to  $0.7 \text{ s}^{-1}$  and  $0.4 \text{ s}^{-1}$  were obtained for  $50 \mu\text{M}$  of **Ru<sub>3</sub>SiPOM** and  $42 \mu\text{M}$  of **Co<sub>4</sub>SiW<sub>9</sub>POM**, respectively. Compound **Ni<sub>4</sub>SiPOM** shows no catalytic activity under same experimental conditions. Based on calculations and catalytic studies, the authors proposed the formation of POM-photosensitizer (POM-PS) complexes as the catalytically active species. A number of control experiments collectively make a strong case that catalysts **Ru<sub>3</sub>SiPOM** and **Co<sub>4</sub>SiW<sub>9</sub>POM** are stable under the experimental conditions. Both dynamic light scattering (DLS) and transmission electron microscopy (TEM) confirmed that no colloidal nanoparticles from decomposition of the POM WOCs are present. Preliminary control experiments also ruled out the possibility that soluble Co species were leaching from a POM WOC as proposed by Stracke and Finke under their quite different (electrochemical) conditions.

Very recently, Sakai and co-workers reported that mono- and dicobalt(III)-containing polyoxomolybdates,  $[\text{CoMo}_6\text{O}_{24}\text{H}_6]^{3-}$  (**CoMoPOM**, Fig. 2(i)) and  $[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4]^{6-}$  (**Co<sub>2</sub>MoPOM**, Fig. 2(j)), catalyze water oxidation (aqueous borate buffer solution at pH 8.0).<sup>114</sup> Under optimal experimental conditions (Table 1, entries 26, 27), the initial TOF and quantum yield ( $\Phi(\text{O}_2)$ ) for **CoMoPOM** are as high as  $0.11 \text{ s}^{-1}$  and 54%, respectively. The corresponding values for **Co<sub>2</sub>MoPOM** are  $0.16 \text{ s}^{-1}$  and 42%, respectively. This paper also provides a thorough stability study that rules out the possible formation of  $\text{CoO}_x$  nanoparticles.

Given these stability studies and those in other publications (see also Section 2c), three points are further strengthened: (1) cobalt centers in all-oxygen ligand environments, including and particularly in POM ligand environments, can be active for water oxidation; (2) that a single Co site in a POM can facilitate multi-electron transfer events; and (3) that cobalt-containing POMs remain molecular WOCs and do not convert

to metal oxide nanoparticles under most conditions for homogeneous catalytic water oxidation.

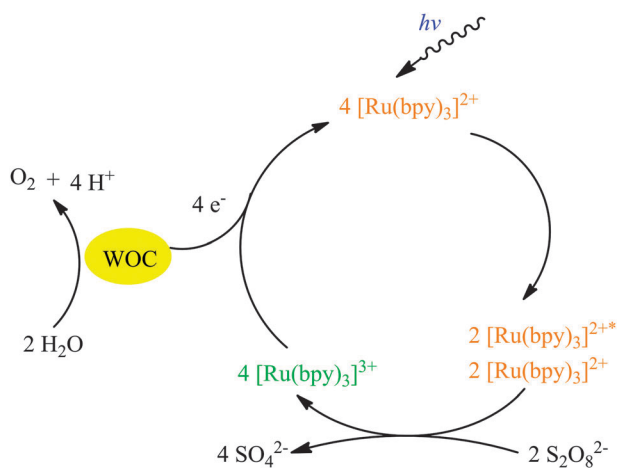
Nickel in appropriate ligand environments should also have water oxidation activity. Harriman et al in their broad spectrum screening of metal oxides for such activity (18 different d- and p-block metal oxides) did report a very low level activity for NiO.<sup>57</sup> Although Patzke et al just reported that  $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2]^{12-}$  (**Ni<sub>4</sub>SiPOM**) has no catalytic water oxidation activity,<sup>243</sup> the Hill group just prepared and thoroughly characterized a pentanickel-containing silicotungstate complex,  $[\text{Ni}_5(\text{OH})_6(\text{OH}_2)_3(\text{Si}_2\text{W}_{18}\text{O}_{66})]^{12-}$  (**Ni<sub>5</sub>SiPOM**, Table 1, entry 12) that appears to be an efficient WOC in both dark ( $[\text{Ru}(\text{bpy})_3]^{3+}$  as oxidant) and light-driven ( $[\text{Ru}(\text{bpy})_3]^{2+}$  as photosensitizer and persulfate as oxidant) reactions.<sup>242</sup> The X-ray structure of **Ni<sub>5</sub>SiPOM** (Fig. 2(f)) reveals the unique geometrical structure of this multi-metal-active-site POM WOC. We write “appears to be an efficient catalyst” because while the results from several techniques are all consistent with **Ni<sub>5</sub>SiPOM** (or another molecular species **Ni<sub>5</sub>SiPOM** converts to) being the actual catalyst and not nickel hydroxide/oxide particles, it is hard to prove this. Interestingly dynamic light scattering (DLS), kinetics and other data all indicate that **Ni<sub>5</sub>SiPOM** largely exists in the medium for the WOC studies (buffered water) as a minimally soluble  $[\text{Ru}(\text{bpy})_3]^{n+}$ -POM ion pair where both the soluble and more abundant precipitated **Ni<sub>5</sub>SiPOM** units likely contribute to the net observed catalytic water oxidation. Under photo-driven conditions, this  $[\text{Ru}(\text{bpy})_3]^{n+}$ -POM system gives a TON of *ca.* 60, corresponding to a quantum yield of *ca.* 3.8%, in the presence of  $2 \mu\text{M}$  **Ni<sub>5</sub>SiPOM**.

## 2b. Mechanistic evaluation of catalytic activity

The most common approaches to evaluate catalytic water oxidation activity are based on the use of strong stoichiometric oxidants such as Ce(IV) ( $E^\circ = 1.72 \text{ V}$ , NHE<sup>244</sup>) or  $[\text{Ru}(\text{bpy})_3]^{3+}$  ( $E^\circ = 1.26 \text{ V}$ , NHE<sup>245</sup>), highly biased anodes (including controlled potential electrolysis studies), or light induced generation of strong oxidants in the presence of a sacrificial electron acceptor. The first method is fairly simple experimentally and usually provides data that are easier to interpret, but it has disadvantages. For example, Ce(IV) can only be used in very strong acid (pH < 1), while  $[\text{Ru}(\text{bpy})_3]^{3+}$  has a lower oxidation potential and is noticeably unstable hydrolytically at pH > 5. In electrocatalytic oxidations the activity is affected by diffusion, double layer effects, ion-pairing, *etc.* In addition, electron transfer between the catalyst molecule and the electrode surface is often very slow. All these issues complicate the interpretation of electrochemical results for catalytic water oxidations.

The  $[\text{Ru}(\text{bpy})_3]^{2+}$ /visible light/persulfate combination has been frequently used as a source of long-lived photogenerated holes (oxidation equivalents). This system has been used in conjunction with WOC studies since the early 1980s,<sup>56,246,247</sup> and these reactions have been studied by several groups, including ours, more recently.<sup>245,247–250</sup>

In the homogeneous light driven water oxidation system (Scheme 1), the triplet metal (Ru)-to-ligand (bpy) charge transfer (<sup>3</sup>MLCT) excited state,  $[\text{Ru}(\text{bpy})_3]^{2+*}$ , is quenched by



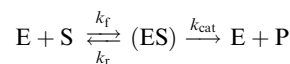
**Scheme 1** Schematic presentation of the homogeneous light-driven water oxidation systems.

$\text{S}_2\text{O}_8^{2-}$  through both bimolecular and unimolecular processes generating  $[\text{Ru}(\text{bpy})_3]^{3+}$  and  $\text{SO}_4^{\bullet-}$ .<sup>240,248–250</sup> The latter radical subsequently oxidizes a second  $[\text{Ru}(\text{bpy})_3]^{2+}$  to  $[\text{Ru}(\text{bpy})_3]^{3+}$  quantitatively.<sup>251</sup> The photogenerated  $[\text{Ru}(\text{bpy})_3]^{3+}$  then functions as the oxidant for water oxidation. Interpreting data obtained in such light driven systems is quite challenging. To date there is no adequate kinetic model to describe the quantum and chemical yields of  $\text{O}_2$ . Therefore it makes little sense to compare such data obtained under different conditions. As an example, we have shown that under identical experimental conditions the quantum and chemical yields of  $\text{O}_2$  depend not only on the shape of the reaction vessels but also on the quality of a glass surface.<sup>240</sup> Since the rate of  $[\text{Ru}(\text{bpy})_3]^{3+}$  generation is proportional to the photon flux (light intensity), the rate of  $\text{O}_2$  formation also increases with photon flux. As a result, the rate of  $\text{O}_2$  formation in light driven systems is directly linked to the quantum yield but not to the TOF. TOF cannot be determined in light driven systems without an adequate kinetic model.

Simultaneous measurement of the kinetics of oxidant consumption and  $\text{O}_2$  formation is one of the most informative and convincing tools to examine the mechanism of catalytic water oxidation reactions, but this is truly hard to accomplish, particularly for rapid WOCs, of which there are now several. The reactions using  $\text{Ce}(\text{IV})$  as an oxidant always take place at high ionic strength, an issue that cannot be ignored. Due to the low stability of  $[\text{Ru}(\text{bpy})_3]^{3+}$ , the catalytic reduction of  $[\text{Ru}(\text{bpy})_3]^{3+}$  should proceed very quickly (within seconds), making it almost impossible to follow the kinetics of  $\text{O}_2$  formation. Many literature studies do not appear to appreciate the above challenges.

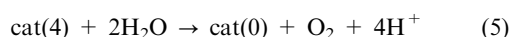
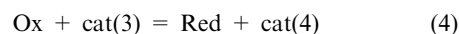
**Definitions and mechanistic issues.** Literature reports of catalytic water oxidation activity usually compare the rates in different systems and report “the most efficient catalyst,” “the fastest catalyst (or the highest TOF)” and even “the best catalyst.” The field could use some clarity on key related terms. The definitions of turnover frequency (TOF) and turnover number (TON) are quite controversial and the numbers reported in the literature are confusing. “IUPAC Compendium of Chemical Terminology” (2011-10-11: Release 2.3, [http://goldbook.iupac.org/]) states that in

catalysis and in enzyme catalysis TON is the number of “molecules reacting per active site in unit time.” In catalysis, TON was introduced as the experimental number calculated as the ratio of product molecules formed per catalyst molecule. Simultaneously, the TON is often defined as the number of moles of substrate that a mole of catalyst can convert before becoming inactivated. We suggest this number would be best referred to as the “maximum achievable turnover number” or “ $\text{TON}_{\text{max}}$ ”.  $\text{TON}_{\text{max}}$  is thus directly related to the stability of the catalyst. The term TOF is commonly defined as the TON per unit time,  $\text{TOF} = \text{d}(\text{TON})/\text{d}t$ . In heterogeneous catalysis TOF is often called “the turnover rate”.<sup>252</sup> In the glossary of terms used in photocatalysis and radiation catalysis recommended by IUPAC,<sup>253</sup> the TOF is defined as the number of photocatalytic cycles per number concentration of the photocatalyst:  $\text{TOF} = (\text{reaction rate})/[\text{cat}]$ , which is the same as  $\text{TOF} = \text{d}(\text{TON})/\text{d}t$ . In this case, TOF appears as an experimental number that is dependent on the experimental conditions, and as such is unsuitable for characterizing the intrinsic properties of the catalyst. In enzymology TOF is defined more rigorously, while ironically TOF is often noted as TON causing additional confusion. Michaelis–Menten kinetics (below) is one of the simplest and best-known models of enzyme kinetics.



where E is an enzyme and S is a substrate. The TOF is unambiguously defined as equal to  $k_{\text{cat}}$ , which is the highest theoretically achievable value,  $\text{TOF}_{\text{max}}$ . This number is independent of reagent concentrations and is an intrinsic property of the reactive site. In contrast to TON, TOF cannot be determined without some knowledge of the reaction rate law. In numerous papers on water oxidation TOF is defined as recommended by IUPAC,  $\text{TOF} = \text{d}(\text{TON})/\text{d}t$  at  $t = 0$ , which is usually lower than  $\text{TOF}_{\text{max}}$ . However, in many cases TOF is not related to  $k_{\text{cat}}$  at all. This is the case, for example, if the formation of the reactive species is the rate limiting step. The term overpotential is also controversial in homogeneous systems. In electrochemistry, this term for water oxidation systems is simply defined as the difference between the applied potential where the electrocatalytic process starts and the thermodynamic potential. In homogeneous systems the open circuit potential can be considered as the applied potential. This potential can be calculated from the Nernst equation provided the concentrations of oxidized and reduced species are known. These concentrations are controlled by the kinetics. As a result, the overpotential in homogeneous systems can be determined based on some knowledge of the reaction kinetics.

The simplest mechanism of water oxidation using a one-electron oxidant, Ox, can be written as eqn (4)–(6):



where Ox is the oxidant, Red is the reduced form of Ox, the number  $i$  in parenthesis of  $\text{cat}(i)$  is the number of electrons withdrawn from the initial oxidation state of the catalyst,



cat(0). Under steady state conditions with respect to catalyst concentrations, one can derive the reaction rate law for O<sub>2</sub> formation,  $r(\text{O}_2)$  and TOF, eqn (7) and (8):

$$r(\text{O}_2) = k_4 k_5 [\text{Ox}][\text{cat}]/(k_5 + k_4[\text{Ox}] + k_{-4}[\text{Red}]) \quad (7)$$

$$\text{TOF} = r(\text{O}_2)/[\text{cat}] = k_4 k_5 [\text{Ox}]/(k_5 + k_4[\text{Ox}] + k_{-4}[\text{Red}]) \quad (8)$$

where [cat] is the total catalyst concentration. The rate constant numbers correspond to the equation number. As seen, the TOF appears to be dependent on rate constants and on both [Ox] and [Red]. If the reaction in eqn (5) is the rate limiting step ( $k_5 \ll k_4[\text{Ox}] + k_{-4}[\text{Red}]$ ), then the initial rate  $r(\text{O}_2)_0 = k_5[\text{cat}]$ . In this case  $r(\text{O}_2)_0/[\text{cat}] = k_5 = \text{TOF}_{\text{max}}$ . Thus, minimum kinetic studies should be performed to determine  $\text{TOF}_{\text{max}}$ . For example, Bonchio *et al.*<sup>222</sup> reported  $\text{TOF} = 450 \text{ h}^{-1}$  ( $0.125 \text{ s}^{-1}$ ) for water oxidation by Ce(IV) in acidic media catalyzed by **Ru<sub>4</sub>SiPOM**. At the same time their kinetic studies give  $r(\text{O}_2)_0/[\text{cat}] = 0.01 \text{ s}^{-1}$ , which is an order of magnitude lower. In our paper,<sup>224</sup> for the same catalyst but at neutral pH with  $[\text{Ru}(\text{bpy})_3]^{3+}$  as an oxidant we obtained  $k_5 = 0.25 \text{ s}^{-1}$  based on fitting of kinetic data to the mechanism in eqn (4)–(6). Interestingly, the overpotentials defined as  $\eta = (E_{\text{ox}}^{\circ} - E^{\circ})$  (see below) for the both systems are almost the same (in the range 0.45–0.5 V), but the TOF is slightly higher at neutral pH. This can be explained by the difference in protonation states of **Ru<sub>4</sub>SiPOM**. Recently, Duan *et al.*<sup>254</sup> described a molecular ruthenium catalyst  $[\text{Ru}(\text{bda})(\text{isoq})_2]$  ( $\text{H}_2\text{bda} = 2,2'$ -bipyridine-6,6'-dicarboxylic acid;  $\text{isoq} = \text{isoquinoline}$ ) for water-oxidation by Ce(IV) with a  $\text{TOF} > 3 \times 10^2 \text{ s}^{-1}$ , which is comparable to that of Photosystem II. In this system an intermediate  $\text{Ru}^{\text{V}}=\text{O}$  dimerizes to form a  $\text{Ru}^{\text{IV}}-\text{OO}-\text{Ru}^{\text{IV}}$  peroxy species. This latter intermediate is oxidized by Ce(IV) into the “ $\text{Ru}^{\text{IV}}$ -superoxy dimer,” which quickly releases O<sub>2</sub>. The reported kinetic data clearly indicate that this dimerization is the rate limiting step. Therefore, the TOF in this system is related to the formation of the O<sub>2</sub>-releasing species, but not to the rate of O<sub>2</sub> formation.

In solution the open circuit electrochemical potential is given in eqn (9):

$$\begin{aligned} E &= E_{\text{ox}}^{\circ} + (RT/F) \log([\text{Ox}]/[\text{Red}]) \\ &= E_{3/4}^{\circ} + (RT/F) \log([\text{cat}(4)]/[\text{cat}(3)]) \end{aligned} \quad (9)$$

where  $E_{\text{ox}}^{\circ}$  and  $E_{3/4}^{\circ}$  are the standard oxidation potentials of Ox/Red and cat(3)/cat(4). The ratios [Ox]/[Red] and [cat(4)]/[cat(3)] are controlled by eqn (4)–(6) and the overpotential in the system is given by eqn (10):

$$\eta = (E_{3/4}^{\circ} - E^{\circ}) + (RT/F) \log(K_4) \quad (10)$$

If the reaction in eqn (5) is the rate limiting step, the overpotential is simply the difference in the two standard electrochemical potentials,  $\eta = (E_{\text{ox}}^{\circ} - E^{\circ})$ . For  $[\text{Ru}(\text{bpy})_3]^{3+}$  at pH 7,  $\eta$  is  $\sim 0.44 \text{ V}$ . The TOF and overpotential are linked to each other, therefore the catalytic activity cannot be characterized by a single number. Recently, Savéant *et al.* came to a similar conclusion in the application to molecular catalysis of electrochemical reactions.<sup>255</sup>

## 2c. Stability of POM WOCs

As noted in Section 1c, the practical issues for a viable WOC are that it be fast, selective and extremely stable.<sup>74–76</sup> In other words, it needs to work very efficiently and for a very long time. The exact nature of the active catalyst is of some practical importance but of much greater intellectual interest. As described above, the issue of whether a soluble complex generates a homogeneous or a heterogeneous catalyst is a topic with a long history.<sup>73</sup> In the case of POM WOCs, many experiments on different complexes by many groups have probed whether an initial POM when dissolved in the reaction medium (typically water) results in homogeneous catalysis (soluble, molecular species account for all the observed water oxidation) or heterogeneous catalysis (particles, films or other insoluble species account for all or most of the observed activity). Unlike all the non-POM soluble WOCs, both the POMs and metal oxide WOCs are stable to oxidative degradation and heat because they are carbon free (no organic ligands). However, the third type of stability, hydrolytic, can and does vary. An intrinsic and deep attraction of POMs and a central part of our experimental program at Emory University to develop POMs as WOCs is that POMs are actually more stable than the corresponding metal oxide mixtures in water in various pH ranges. Thus one wants to design POM WOCs that are thermodynamically stable in water at the pH where they will be used as catalysts, whether they be totally in solution or partly precipitated as, for example, minimally soluble salts with photosensitizers as in the case with the penta-nickel POM.<sup>242</sup> This is true, of course, if the intact molecular form of the POM is a better catalyst (faster, more selective, less subject to poisoning) than a corresponding metal oxide film. Indeed most homogenous catalysts turn over much faster than their heterogeneous counterparts per metal center because a soluble species effectively has the highest possible concentration (or in heterogeneous catalysis terms, “surface area”).

The first POM WOC developed,  $[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  (**Ru<sub>4</sub>SiPOM**) has been used extensively by the groups of Hill, Bonchio and others and to date there is no evidence in any experiment that it ever hydrolyses to form metal oxide (films, particles) under catalytic water oxidation conditions. However, this is not the case for  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (**Co<sub>4</sub>PPOM**), the first POM WOC composed entirely of earth abundant elements. **Co<sub>4</sub>PPOM** was first reported to catalyze the efficient oxidation of water by  $[\text{Ru}(\text{bpy})_3]^{3+}$  to oxygen in pH 7 aqueous phosphate buffer.<sup>239</sup> Seven lines of experimental evidence were provided that constituted very strong evidence that **Co<sub>4</sub>PPOM** functions as a homogeneous catalyst and does not decompose to form metal oxide.<sup>239</sup> Subsequently, Stracke and Finke showed that under quite different conditions (electrochemical oxidation using a graphite anode with greatly different catalyst concentrations, but in the same pH 7 phosphate buffer), **Co<sub>4</sub>PPOM** itself is not an active WOC. Instead, it functions solely as precursor for a cobalt oxide film that forms on the graphic anode.<sup>256</sup> This film is the actual catalyst. These investigators also conducted several experiments that provided a compelling case that under *their* conditions **Co<sub>4</sub>PPOM** does exactly what they report it does. Both studies are very complete and it is very



hard to argue that either is incorrect. A reason this is an issue, is that pH 7 is where **Co<sub>4</sub>PPOM** becomes hydrolytically unstable, and the thermodynamically stable form of these elements in water changes from POM to metal oxide. The POM (soluble) = metal oxide (insoluble) equilibrium is also influenced by the presence of some anions, like phosphate, which can form a more stable solid phase than the corresponding oxide. In both these studies, phosphate is present. The concern is that Stracke and Finke extrapolated their findings under their different conditions to our work and implied that **Co<sub>4</sub>PPOM** is not a WOC in general. This was not defensible.

These studies have led to much speculation and the positions of many groups that have examined these initial studies on whether **Co<sub>4</sub>PPOM** is a homogeneous catalyst or only a catalyst precursor fall approximately into three categories: (1) it is merely a pre catalyst for the true catalyst under both electrochemical and homogeneous conditions;<sup>256–258</sup> (2) it is not stable under electrochemical conditions but is a functioning molecular catalyst under homogeneous dark or light driven systems<sup>54,70,114,243,259,260</sup> (3) it is not stable under electrochemical conditions and its stability under homogeneous conditions remains unclear.<sup>73,232,261–265</sup> A publication that just appeared weighs in on the issue with further experimental evidence under light-driven conditions.<sup>266</sup> This study rules out Co(II) as a precursor to CoO<sub>x</sub> as hypothesized by Stracke and Finke.<sup>256</sup> They, like we and other groups, see no particles of metal oxide by dynamic light scattering and other quite definitive techniques after use of **Co<sub>4</sub>PPOM** in homogeneous catalytic water oxidation. Since we and others can also account for what appears to be 100% of the original **Co<sub>4</sub>PPOM** after use in catalytic water oxidation, the hypothesis that **Co<sub>4</sub>PPOM** is in equilibrium with another more active but clearly soluble, molecular species is credible. There is quite compelling evidence that **Co<sub>4</sub>PPOM** does in fact remain in solution as a soluble WOC near its pH limit.<sup>234</sup> However, it is also quite clear that minor changes in conditions near the pH where **Co<sub>4</sub>PPOM** becomes thermodynamically unstable must be conducted with great care, and further studies with this particular POM WOC are warranted.

Far more active POM WOCs have been developed that are more hydrolytically stable in base. These will be reported shortly. However, one ultimate goal is to formulate soluble, extremely fast POM WOCs that are thermodynamically stable hydrolytically in strong base because this is one engineering paradigm for solar water splitting using cell, including photoelectrochemical cell, architectures.

### 3. Polyoxometalates as chromophores

POMs have a rich and well studied photochemistry dating back to 1916.<sup>267</sup> A few reviews of POM photoredox chemistry have been published,<sup>268–270</sup> and a more recent one notes some more recent work.<sup>271</sup> The great majority of POM photochemistry involves photoexcitation of the intra-POM oxygen-to-tungsten charge transfer (CT) bands of conventional (d<sup>0</sup> configuration) POMs.<sup>272</sup> These O<sub>2p</sub> to W<sub>5d</sub> (or Mo<sub>4d</sub>) LMCT excited states react primarily by abstracting hydrogen atoms from C–H substrates<sup>273–276</sup> and the resulting reduced POMs are reoxidized either by hydrogen evolution,<sup>277–282</sup> a process that is catalyzed by Pt(0) in various

forms, or by reaction with O<sub>2</sub>/air.<sup>269,283–285</sup> A wide range of organic substrates<sup>207,208,286,287</sup> is readily oxidized in reasonably high quantum yields using ultraviolet or high-energy visible light (d<sup>0</sup> POMs only absorb at these wavelengths). These intra-POM CT excited states are sufficiently reactive that they abstract hydrogen atoms from unactivated C–H bonds.<sup>288,289</sup> A diversity of C–H bond functionalized products can be formed depending on the conditions. Indeed, both the regiochemistry and the nature of the functional group associated with the unactivated C–H bond cleavage can be widely controlled.<sup>288–295</sup>

The effects of POM protonation on these photo-induced POM-catalyzed organic substrate functionalization processes have been studied. When high potential or protonated low-potential POMs are photoexcited, the intermediate organic radicals produced by the initial hydrogen atom abstraction are oxidized by these POMs to carbocations; whereas, when unprotonated low-potential POMs are photoexcited, these intermediate radicals are not oxidized to carbocations.<sup>193,276,290,292</sup>

Unfortunately these oxygen-to-tungsten CT excited states of conventional POMs do not involve long-range charge transfer and they are quite short lived,<sup>272,296–298</sup> so they do not hold much promise as potential photosensitizers or chromophores for absorption of sunlight. Some complexes involving organic donors, other than [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, and POM acceptors have been prepared and well characterized,<sup>299–302</sup> but these also exhibit short-lived excited states.<sup>300,303</sup> In addition the reduced forms of POMs, frequently called “heteropoly blues” resulting from broad d–d and intervalence charge transfer (IVCT) absorptions (typically in the range of 600 to 1000 nm rendering them blue)<sup>304–311</sup> also exhibit little promising photo-redox chemistry.

POMs that absorb visible-light or exhibit long-range CT in the excited state are very rare: research in this area is in its infancy. To this end, several groups have prepared outer sphere CT species in the form of ion pairs between cationic chromophores and POM electron acceptors.<sup>205,208,210,312–314</sup> The inter-ion electron transfer is not efficient in the ion pairs and the structural relationship between the two ionic units is disrupted upon dissolution in a suitable solvent. Several groups have synthesized POMs with covalently attached pyrene, ruthenium and metalloporphyrin chromophores and studied their photophysical properties.<sup>195,315–320</sup> The relative dye-POM positions are somewhat confined in these hybrid species, and thus exhibit more pronounced inter-unit interactions than in the ion pair POM systems above. However, these POM-based hybrid compounds are quite challenging to make, even in modest quantities. More recently, the Feng group demonstrated that a Tin(II)-based POM absorbs visible-light and can evolve hydrogen under appropriate conditions.<sup>321</sup>

Incentivized with the realization that while organic chromophores will likely have sufficient stability to afford adequately long-lived photovoltaic devices, including dye-sensitized solar cells (DSSCs), this probably is not true for solar fuel generation systems. For the latter, the bar for stability is far higher because oxidizing and other reactive intermediates in the fuel forming processes will thermodynamically and kinetically destroy most if not all organic structure before the requisite number of turnovers to define commercial viability (again, TON as high as 10<sup>9</sup>).

With this concern in mind, the Emory team prepared a system with multiple coordinate covalent bonds between the donor and acceptor thus dictating a precise structural orientation between the two. They wanted to take advantage of the strong electron acceptor properties of POMs and thus covalently bound a  $[\text{Re}(\text{CO})_3]^+$  electron donor group to a Wells–Dawson POM derivative electron acceptor. The resulting complex,  $[\text{P}_4\text{W}_{35}\text{O}_{124}\{\text{Re}(\text{CO})_3\}_2]^{16-}$ ,<sup>322</sup> was characterized by X-ray crystallography and several other methods and exhibits high visible-region absorptivity ( $\epsilon_{470\text{ nm}} = 4000\text{ M}^{-1}\text{cm}^{-1}$  in water) resulting from a  $\text{Re}^1$ -to-POM CT transition. This metal-to-polyoxometalate charge transfer (MPCT) is a new category of transition, reminiscent but distinct from the (metal–oxygen–metal) MMCT chromophores developed by the Frei group,<sup>59,323–325</sup> and should be general for a huge class of synthetically modifiable POMs. Computational studies confirmed transient absorption measurements in the visible and mid-IR regions indicating that upon absorption of visible light by  $[\text{P}_4\text{W}_{35}\text{O}_{124}\{\text{Re}(\text{CO})_3\}_2]^{16-}$ , there is an instantaneous ( $<50\text{ fs}$ ) MPCT process involving electron transfer from the  $\text{Re}(\text{i})$  center into the POM ligand.<sup>322</sup>

#### 4. Conclusions

This review provides ample evidence that POMs, as robust yet extensively tunable, molecular systems, have considerable promise in the development multi-electron-transfer catalysis, chromophores and other key components of solar fuel generation systems.

#### Acknowledgements

We thank the Department of Energy, Office of Basic Energy Sciences (grant number: DE-FG02-07ER15906) for funding this work.

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