

Communication

## Activity and Stability of the Tetramanganese Polyanion $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ during Electrocatalytic Water Oxidation

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**Abstract:** In natural photosynthesis, the oxygen evolving center is a tetranuclear manganese cluster stabilized by amino acids, water molecules and counter ions. However, manganese complexes are rarely exhibiting catalytic activity in water oxidation conditions. This is also true for the family of water oxidation catalysts (WOCs) obtained from POM chemistry. We have studied the activity of the tetranuclear manganese POM  $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  ( $\text{Mn}_4$ ), the manganese analog of the well-studied  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  ( $\text{Co}_4$ ), one of the fastest and most interesting WOC candidates discovered up to date. Our electrocatalytic experiments indicate that  $\text{Mn}_4$  is indeed an active water oxidation catalysts, although unstable. It rapidly decomposes in water oxidation conditions. Bulk water electrocatalysis shows initial activities comparable to those of the cobalt counterpart, but in this case current density decreases very rapidly to become negligible just after 30 min, with the appearance of an inactive manganese oxide layer on the electrode.

**Keywords:** polyoxometalates; electrocatalysis; water oxidation

## 1. Introduction

Water oxidation catalysis is currently one of the hot topics in chemistry research [1–3], since it is regarded as the bottleneck in the development of an artificial photosynthesis scheme [4–6]. Fuels production by harvesting solar energy to reduce a substrate (as protons to hydrogen) needs to occur concomitant to the oxidation of water into oxygen. If this second process is not fast enough and energy efficient, cost-effective solar fuels production will never become a technological reality.

Polyoxometalates (POMs) are some of the most promising electrocatalysts to promote water oxidation [7,8] due to their dual nature. Being molecular species, POMs possess all advantages of homogeneous catalysts, being fast, monodispersed and easy to process. At the same time, as fragments of metal oxides, POMs also exhibit some of the advantages of heterogeneous catalysts, as they possess the right catalytic active sites, and appear to be highly robust and stable in water oxidation conditions [9].

The first POM reported as a water oxidation catalyst (WOC) was the tetraruthenium polyanion  $[(\text{SiW}_{10}\text{O}_{36})_2\text{Ru}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^{9-}$  [10,11]. Although very fast and rugged [12–15], its noble metal content precluded to envision technological impact since realization of artificial photosynthesis will require inexpensive and readily-available catalysts.

The breakthrough in the area appeared when the tetracobalt POM  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (**Co<sub>4</sub>**), obtained from earth abundant metals, was reported to be one of the fastest WOCs up to date [16,17]. Some studies suggested that this POM may not be stable in water oxidation conditions [18–20]. Although this is true for certain conditions, and it can put into question the quantification of its catalytic activity, it is important to note that the genuine WOC activity of **Co<sub>4</sub>** has been confirmed beyond any reasonable doubt [21–23], and corroborated even by the most (initially) critical research teams [24]. Following these results, several related POMs have shown WOC activity [7,25–29], most of them containing Co<sup>II</sup> as water-ligated active center.

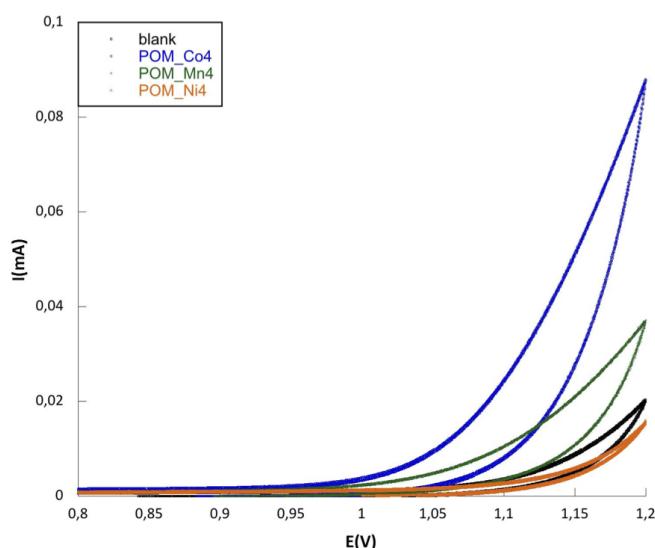
Artificial photosynthesis takes inspiration from natural photosynthesis in green plants and algae, where a tetramanganese cluster is responsible for the catalysis of the water oxidation reaction [30–33]. However, Mn-containing POMs have not been so successful. There is only one Mn-based example, reported very recently [34]. This trend of few Mn examples is not exclusive of POMs [1], and even if one considers heterogeneous catalysts, Mn oxide is much less active than the corresponding Co or Ni analogs [35]. Still, the use of Mn is attractive because it is earth abundant and relatively nontoxic when compared with the other more active metal-based catalysts.

In the search for Mn-containing POMs which could exhibit WOC activity we decided to test the Mn<sup>II</sup> structural equivalent of the tetra cobalt WOC reported by Hill *et al.* [16]. The water electrochemistry of this polyanion  $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (**Mn<sub>4</sub>**) confirms its activity as a water oxidation catalysts, albeit its intrinsic instability in water oxidation conditions.

## 2. Results and Discussion

**Mn<sub>4</sub>** was prepared as a mixed Na/K salt following literature procedure. The structure of the polyanion consists of rhomblike tetranuclear cluster of MnO<sub>6</sub> octahedra sharing edges encapsulated by two lacunary Keggin-type [PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> units (Figure 3b). All bridges between Mn atoms are oxo groups from WO<sub>6</sub> or PO<sub>4</sub> polyhedra. Two terminal water molecules complete the coordination positions of the Mn centers in the long diagonal of the rhomb.

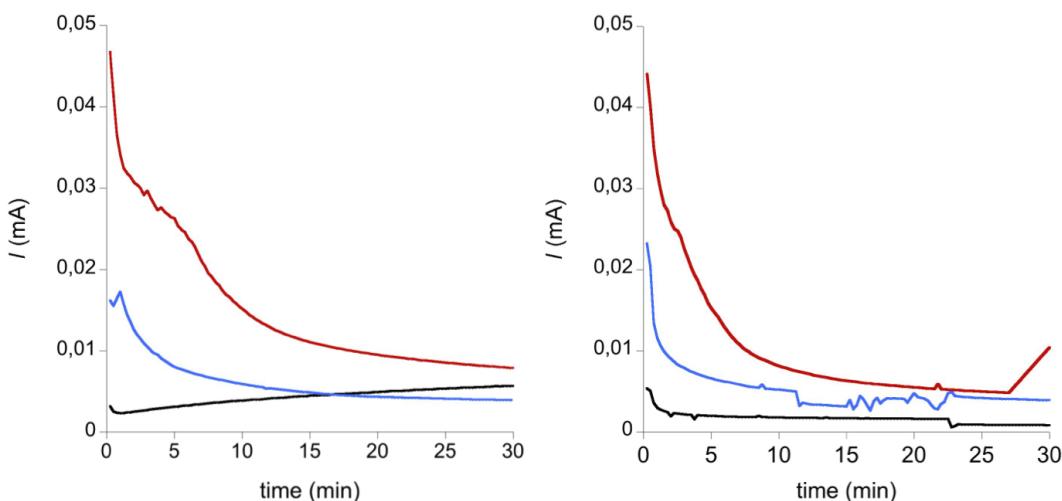
We carried out cyclic voltammetry experiments in a pH 7 sodium phosphate buffer (NaP<sub>i</sub>, 50 mM) solution with a amorphous carbon disc anode, a Pt wire cathode and a Ag/AgCl (NaCl 3 M) reference electrode (Figure 1). In the presence of **Mn<sub>4</sub>** (1 mM) a significant catalytic water oxidation wave is observed above 1.0 V, which is accompanied by significant gas bubbling at the anode. This suggests that **Mn<sub>4</sub>** is indeed a WOC at neutral pH. The catalytic activity appears to be slower In comparison with the activity of **Co<sub>4</sub>** in the same conditions, since the **Mn<sub>4</sub>**-catalyzed wave appears below the **Co<sub>4</sub>** cyclic voltammetry at all potentials. It is also worthy to mention that no pre-catalytic features are observed in the data, indicating that no additional redox processes occur before catalysis.



**Figure 1.** Cyclic voltammetry in a pH 7 sodium phosphate buffer (50 mM) water solution as electrolyte: 1.0 mM **Co<sub>4</sub>** (blue line); 1.0 mM **Mn<sub>4</sub>** (green line); blank (black line). *E* reported vs. Ag/AgCl (3 M) reference electrode.

We carried out bulk water electrolysis experiments under stirring in a two-chamber cell with both chambers connected through a glass frit (Figure 2). As anode and cathode we used FTO-coated glass (1 cm × 1 cm) and Pt mesh electrodes, respectively. The Ag/AgCl (NaCl 3 M) reference electrode was located close the anode, in the anodic compartment. Negligible current values were obtained when an anodic overpotential of ≈ 600 mV was applied (1.40 V vs. NHE) to this set-up with a pH 7 sodium phosphate buffer (NaP<sub>i</sub>, 50 mM) solution with NaNO<sub>3</sub> (1 M) as electrolyte in the absence of a catalyst. The addition of **Mn<sub>4</sub>** (1 mM) to the anodic compartment resulted in rapid gas evolution, with a fast current increase reaching typical currents (*i*) over 0.03 mA. After a short induction time, *i* keeps decreasing slowly to reach negligible values after just 30 min. During this time, the solution maintains essentially its original orange color, but a thin brown film grows on the anode. Chemical

analysis of this film, which exhibited amorphous X-ray powder patterns, showed that manganese is the only metal significantly present. This suggests that, while the POM is stable and active in solution, there is a second process where it rapidly decomposes under an oxidation potential to yield a manganese oxide phase that grows on the electrode. This phase appears to be inactive as a WOC, and catalysis stops when the access of the remaining  $\text{Mn}_4$  in solution to the electrode is blocked by this film. Indeed, the as-used electrode does not show any significant remnant catalytic activity. A similar process was observed for other Co-containing POM-based WOCs [18], although the deposited Co-oxide is a highly active WOC. The inactivity of the Mn-oxide film observed in our case makes easier to identify the genuine catalytic activity of  $\text{Mn}_4$ . Although mixed valence  $\text{MnO}_x$  are active WOCs [36–38], the  $\text{MnO}_2$  phase is inactive [39]. Thus, this should be the major species in the deposited films. The formation of this oxidized  $\text{MnO}_x$  film precludes quantitative oxygen production during this water electrolysis.



**Figure 2.** (a) Bulk water electrolysis under an applied anodic potential of 1.40 V /vs. NHE) with an fluorine-doped tin oxide (FTO) anode and Pt mesh cathode in a pH 7 sodium phosphate buffer (50 mM) water solution as electrolyte with 1.0 mM  $\text{Mn}_4$  (red line); a consecutive experiment with the as-used electrode in a  $\text{Mn}_4$ -free electrolyte solution (blue); blank (black line). (b) analogous experiment with addition of bpy(10 mM).

In Co-containing POMs, the formation of metal-oxide films has been assigned to the solution equilibria of the POMs, and not to a redox instability at the electrode [23]. Chelating agents able to trap traces of aqueous  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  ( $\text{M}^{2+} = \text{Co}^{2+}$ ) generated in solution have been very effective to prevent the formation of such oxides. Unfortunately, the same strategy was not successful to prevent formation of the corresponding oxide in this case. Analogous bulk water electrolysis experiment in the presence of 2,2'-bipyridyl showed even faster catalyst decomposition (Figure 2b), suggesting this tetra manganese POM is not redox stable.

In other homogeneous WOCs their incorporation into a heterogeneous matrix has significantly improved their stability, while maintaining their catalytic activity [40]. Following the same strategy, we incorporated the insoluble  $\text{Cs}_{10}[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \times \text{H}_2\text{O}$  salt into an amorphous carbon paste anode. However, the incorporation of the Cs- $\text{Mn}_4$  component showed no effect in the catalytic current, indicating that  $\text{Mn}_4$  is also unstable in such conditions.

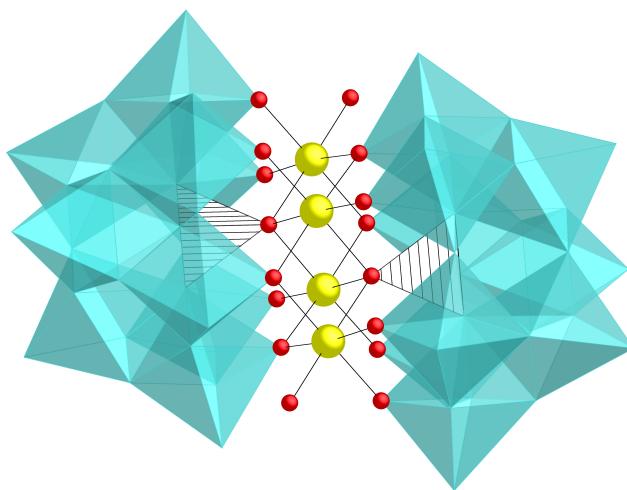
### 3. Experimental Section

#### 3.1. Materials and Instrumentation

All reagents were purchased from Sigma-Aldrich (Madrid, Spain) (>99% purity) and used without further purification. Metal content in POM salts was analyzed with an Environmental Scanning Electron Microscope JEOL-JMS6400 equipped with an Oxford Instruments X-ray elemental analyzer. Thermogrammetry was performed with power samples using a TGA/SDTA851 Mettler Toledo with MT1 microbalance.

#### 3.2. Synthesis and Characterization

**Co<sub>4</sub>** and **Mn<sub>4</sub>** were prepared from optimized literature methods as alkali salts [41,42]. The compounds were recrystallized from water, collected by filtration, dried in vacuum and characterized by IR spectroscopy. The counter cations and solvent content were determined by EDAX microanalysis and thermogravimetry, respectively. The molecular formulas are: Na<sub>5</sub>K<sub>5</sub>[Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] 31H<sub>2</sub>O ( $M_w = 5599.04$ ) and Na<sub>5</sub>K<sub>5</sub>[Mn<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] 31H<sub>2</sub>O ( $M_w = 5583.08$ ). The molecular structure of these polyanions is represented in Figure 3.



**Figure 3.** Molecular structure of the  $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (**Mn<sub>4</sub>**) polyoxometalate.

#### 3.3. Electrochemistry

Bulk water electrolysis were carried out with stirring in a two-chamber cell, with a porous frit connecting both chambers. In one chamber we placed a Pt mesh counter electrode, and in the other chamber a fluorine-doped tin oxide (FTO)-coated glass working electrode and a Ag/AgCl (NaCl 3 M) reference electrode. All potentials are reported *versus* NHE ( $E = E_{obs} + 0.208$ ). Data were collected with a Biologic SP-150 potentiostat. Typical electrolysis experiments were carried out in a sodium phosphate (NaP<sub>i</sub>) buffer pH = 7 solution with NaNO<sub>3</sub> (1 M) as electrolyte. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument.

#### 4. Conclusions

Electrochemistry data of a  $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  at pH = 7 confirms its genuine activity of this POM to promote water oxidation. Nevertheless, its activity is lower when compared with the Co counterpart and, more significant, its stability is poor. During electrocatalytic water splitting,  $\text{Mn}_4$  decomposition products (oxides) deposit on the anode precluding the catalytic activity. After a few minutes, catalysis becomes negligible, reaching values identical to those of the bare electrodes.

These results suggest that, although chosen by natural evolution, Mn may not be the best option for the development of water oxidation catalysts. In POMS, and also in other homogeneous catalysts, Mn-based WOCs appear to be intrinsically unstable during water oxidation [43]. In living entities, the instability of Mn WOCs may be an advantage, since it allows for easier self-repair mechanism in photosystem II. However, this is an important disadvantage when developing working devices.

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#### Author Contributions

JRGM proposed the concept. JRGM and SGF designed the experiments. SGF and JSL performed the experiments. All authors analyzed the data and wrote the manuscript.

#### Conflicts of Interest

The authors declare no conflict of interest.

#### References

1. Spiccia, L.; Singh, A. Water oxidation catalysts based on abundant 1st row transition metals. *Coord. Chem. Rev.* **2013**, *257*, 2607–2622.
2. Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. The mechanism of water oxidation: From electrolysis via homogeneous to biological catalysis. *ChemCatChem* **2010**, *2*, 724–761.
3. Galan-Mascaros, J.R. Water oxidation at electrodes modified with earth-abundant transition-metal catalysts. *ChemElectroChem* **2015**, *2*, 37–50.
4. McKone, J.R.; Lewis, N.S.; Gray, H.B. Will solar-driven water-splitting devices see the light of day? *Chem. Mater.* **2014**, *26*, 407–414.
5. Barber, J. Photosynthetic energy conversion: Natural and artificial. *Chem. Soc. Rev.* **2009**, *38*, 185–196.
6. Walter, M.G.; Warren, E.L.; McKone, J.R.; Boettcher, S.W.; Mi, Q.; Santori, E.A.; Lewis, N.S. Solar water splitting cells. *Chem. Rev.* **2010**, *110*, 6446–6473.

7. Lv, H.; Geletii, Y.V.; Zhao, C.; Vickers, J.W.; Zhu, G.; Luo, Z.; Song, J.; Lian, T.; Musaev, D.G.; Hill, C.L. Polyoxometalate water oxidation catalysts and the production of green fuel. *Chem. Soc. Rev.* **2012**, *41*, 7572–7589.
8. Streb, C. New trends in polyoxometalate photoredox chemistry: From photosensitisation to water oxidation catalysis. *Dalton Trans.* **2012**, *41*, 1651–1659.
9. Hill, C.L. Progress and challenges in polyoxometalate-based catalysis and catalytic materials chemistry. *J. Mol. Catal.* **2007**, *262*, 2–6.
10. Geletii, Y.V.; Botar, B.; Kögerler, P.; Hillesheim, D.A.; Musaev, D.G.; Hill, C.L. An all-inorganic, stable, and highly active tetraruthenium homogeneous catalyst for water oxidation. *Angew. Chem. Int. Ed.* **2008**, *47*, 3896–3899.
11. Sartorel, A.; Miro, P.; Salvadori, E.; Romain, S.; Carraro, M.; Scorrano, G.; di Valentin, M.; Llobet, A.; Bo, C.; Bonchio, M. Water oxidation at a tetraruthenate core stabilized by polyoxometalate ligands: experimental and computational evidence to trace the competent intermediates. *J. Am. Chem. Soc.* **2009**, *131*, 16051–16052.
12. Guo, S.X.; Liu, Y.; Lee, C.Y.; Bond, A.M.; Zhang, J.; Geletii, Y.V.; Hill, C.L. Graphene-supported  $[\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  for highly efficient electrocatalytic water oxidation. *Energy Environ. Sci.* **2013**, *6*, 2654–2663.
13. Orlandi, M.; Argazzi, R.; Sartorel, A.; Carraro, M.; Scorrano, G.; Bonchio, M.; Scandola, F. Ruthenium polyoxometalate water splitting catalyst: Very fast hole scavenging from photogenerated oxidants. *Chem. Commun.* **2010**, *46*, 3152–3154.
14. Toma, F.M.; Sartorel, A.; Iurlo, M.; Carraro, M.; Parisse, P.; Maccato, C.; Rapino, S.; Rodriguez Gonzalez, B.; Amenitsch, H.; da Ros, T.; *et al.* Efficient water oxidation at carbon nanotube-polyoxometalate electrocatalytic interfaces. *Nat. Chem.* **2010**, *2*, 826–831.
15. Besson, C.; Huang, Z.; Geletii, Y.V.; Lense, S.; Hardcastle, K.I.; Musaev, D.G.; Lian, T.; Proust, A.; Hill, C.L.  $\text{Cs}_9[(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ru}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]$ , a new all-inorganic, soluble catalyst for the efficient visible-light-driven oxidation of water. *Chem. Commun.* **2010**, *46*, 2784–2786.
16. Yin, Q.; Tan, J.M.; Besson, C.; Geletii, Y.V.; Musaev, D.G.; Kuznetsov, A.E.; Luo, Z.; Hardcastle, K.I.; Hill, C.L. A fast soluble carbon-free molecular water oxidation catalyst based on abundant metals. *Science* **2010**, *328*, 342–345.
17. Huang, Z.; Luo, Z.; Geletii, Y.V.; Vickers, J.W.; Yin, Q.; Wu, D.; Hou, Y.; Ding, Y.; Song, J.; Musaev, D.G.; *et al.* Efficient light-driven carbon-free cobalt-based molecular catalyst for water oxidation. *J. Am. Chem. Soc.* **2011**, *133*, 2068–2071.
18. Stracke, J.J.; Finke, R.G. Electrocatalytic water oxidation beginning with the cobalt polyoxometalate  $[\text{Co}_4](\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ : Identification of Heterogeneous  $\text{CoO}_x$  as the dominant catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 14872–14875.
19. Stracke, J.J.; Finke, R.G. Water oxidation catalysis beginning with  $2.5 \mu\text{M} [\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ : Investigation of the true electrochemically driven catalyst at  $\geq 600 \text{ mV}$  overpotential at a glassy carbon electrode. *ACS Catal.* **2013**, *3*, 1209–1219.
20. Natali, M.; Berardi, S.; Sartorel, A.; Bonchio, M.; Campagna, S.; Scandola, F. Is  $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$  a genuine molecular catalyst in photochemical water oxidation? Answers from time-resolved hole scavenging experiments. *Chem. Commun.* **2012**, *48*, 8808–8810.

21. Vickers, J.W.; Lv, H.; Sumiliner, J.M.; Zhu, G.; Luo, Z.; Musaev, D.G.; Geletii, Y.V.; Hill, C.L. Differentiating homogeneous and heterogeneous water oxidation catalysis: Confirmation that  $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$  is a molecular water oxidation catalyst. *J. Am. Chem. Soc.* **2013**, *135*, 14110–14118.
22. Schiwon, R.; Klingan, K.; Dau, H.; Limberg, C. Shining light on integrity of a tetracobalt-polyoxometalate water oxidation catalyst by X-ray spectroscopy before and after catalysis. *Chem. Commun.* **2013**, *50*, doi:10.1039/c3cc46629a.
23. Goberna-Ferron, S.; Vigara, L.; Soriano-López, J.; Galán-Mascarós, J.R. Identification of a nonanuclear  $\text{Co}_9^{\text{II}}$  polyoxometalate cluster as a homogeneous catalyst for water oxidation. *Inorg. Chem.* **2012**, *51*, 11707–11715.
24. Stracke, J.J.; Finke, R.G. Water oxidation catalysis beginning with  $\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2^{10-}$  when driven by the chemical oxidant ruthenium(III)tris(2,2'-bipyridine): Stoichiometry, kinetic, and mechanistic studies en route to identifying the true catalyst. *ACS Catal.* **2014**, *4*, 79–89.
25. Song, F.; Ding, Y.; Ma, B.; Wang, C.; Wang, Q.; Du, X.; Fua, S.; Song, J.  $\text{K}_7[(\text{CoCo}^{\text{II}})\text{Co}^{\text{III}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]$ : a molecular mixed-valence Keggin polyoxometalate catalyst of high stability and efficiency for visible light-driven water oxidation. *Energy Environ. Sci.* **2013**, *6*, 1170–1184.
26. Zhu, G.; Glass, E.N.; Zhao, C.; Lv, H.; Vickers, J.W.; Geletii, Y.V.; Musaev, D.G.; Song, J.; Hill, C.L. A nickel containing polyoxometalate water oxidation catalyst. *Dalton Trans.* **2012**, *41*, 13043–13049.
27. Cao, R.; Ma, H.; Geletii, Y.V.; Hardcastle, K.I.; Hill, C.L. Structurally characterized iridium(III)-containing polytungstate and catalytic water oxidation activity. *Inorg. Chem.* **2009**, *48*, 5596–5598.
28. Zhu, G.; Geletii, Y.V.; P., K.; Schilder, H.; Song, J.; Lense, S.; Zhao, C.; I., H.K.; Musaev, D.G.; Hill, C.L. Water oxidation catalyzed by a new tetracobalt-substituted polyoxometalate complex:  $[\{\text{Co}_4(\mu\text{-OH})(\text{H}_2\text{O})_3\}(\text{Si}_2\text{W}_{19}\text{O}_{70})]^{11-}$ . *Dalton Trans.* **2012**, *41*, 2084–2090.
29. Lv, H.; Song, J.; Geletii, Y.V.; Vickers, J.W.; Sumiliner, J.M.; Musaev, D.G.; Kögerler, P.; Zhuk, P.F.; Bacsa, J.; Zhu, G.; *et al.* An exceptionally fast homogeneous carbon-free cobalt-based water oxidation catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 9268–9271.
30. Suga, M.; Akita, F.; Hirata, K.; Ueno, G.; Murakami, H.; Nakajima, Y.; Shimizu, T.; Yamashita, K.; Yamamoto, M.; Ago, H.; *et al.* Native structure of photosystem II at 1.95 Å resolution viewed by femtosecond X-ray pulses. *Nature* **2015**, *517*, 99–103.
31. Kern, J.; Alonso-Mori, R.; Hellmich, J.; Tran, R.; Hattne, J.; Laksmono, H.; Glöckner, C.; Echols, N.; Sierra, R.G.; Sellberg, J.; *et al.* Room temperature femtosecond X-ray diffraction of photosystem II microcrystals. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 9721–9726.
32. Umena, Y.; Kawakami, K.; Shen, J.R.; Kamiya, N. Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. *Nature* **2011**, *473*, 55–60.
33. Ferreira, K.N.; Iverson, T.M.; Maghlaoui, K.; Barber, J.; Iwata, S. Architecture of the photosynthetic oxygen-evolving center. *Science* **2004**, *303*, 1831–1838.

34. Al-Oweini, R.; Sartorel, A.; Bassil, B.S.; Natali, M.; Berardi, S.; Scandola, F.; Kortz, U.; Bonchio, M. Photocatalytic water oxidation by a mixed-valent  $Mn_3^{III}Mn^{IV}O_3$  manganese oxo core that mimics the natural oxygen-evolving center. *Angew. Chem. Int. Ed.* **2014**, *53*, 11182–11185.
35. Zaharieva, I.; Chernev, P.; Risch, M.; Klingan, K.; Kohlhoff, M.; Fischer, A.; Dau, H. Electrosynthesis, functional, and structural characterization of a water-oxidizing manganese oxide. *Energy Environ. Sci.* **2012**, *5*, 7081–7089.
36. Wiechen, M.; Najafpour, M.M.; Allakhverdiev, S.I.; Spiccia, L. Water oxidation catalysis by manganese oxides: Learning from evolution. *Energy Environ. Sci.* **2014**, *7*, 2203–2212.
37. Kuo, C.H.; Mosa, I.M.; Poyraz, A.S.; Biswas, S.; El-Sawy, A.M.; Song, W.; Luo, Z.; Chen, S.Y.; Rusling, J.F.; He, J.; *et al.* Robust mesoporous manganese oxide catalysts for water oxidation. *ACS Catal.* **2015**, *5*, 1693–1699.
38. Najafpour, M.M.; Moghaddam, A.N.; Dau, H.; Zaharieva, I. Fragments of layered manganese oxide are the real water oxidation catalyst after transformation of molecular precursor on clay. *J. Am. Chem. Soc.* **2014**, *136*, 7245–7248.
39. Zaharieva, I.; Chernev, P.; Risch, M.; Klingan, K.; Kohlhoff, M.; Fischer, A.; Dau, H. Electrosynthesis, functional, and structural characterization of a water-oxidizing manganese oxide. *Energy Environ. Sci.* **2012**, *5*, 7081–7089.
40. Soriano-López, J.; Goberna-Ferron, S.; Vigara, L.; Carbó, J.J.; Poblet, J.M.; Galan-Mascaros, J.R. Cobalt polyoxometalates as heterogeneous water oxidation catalysts. *Inorg. Chem.* **2013**, *52*, 4753–4755.
41. Weakley, T.J.R.; Evans, H.T.; Showell, J.S.; Tourne, G.F.; Tourne, C.M. 18-Tungstotetracobaltato(II)diphosphate and related anions. A novel structural class of heteropolyanions. *Chem. Commun.* **1973**, 139–140.
42. Gómez Garcia, C.; Coronado, E.; Gomez-Romero, P.; Casan-Pastor, N. A tetrานuclear rhomblike cluster of manganese(II). Crystal structure and magnetic properties of the heteropoly complex  $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2] \cdot 20H_2O$ . *Inorg. Chem.* **1993**, *32*, 3378–3381.
43. Hocking, R.K.; Brimblecombe, R.; Chang, L.Y.; Singh, A.; Cheah, M.H.; Glover, C.; Casey, W.H.; Spiccia, L. Water-oxidation catalysis by manganese in a geochemical-like cycle. *Nat. Chem.* **2011**, *3*, 461–466.

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