

Bilateral energy conference
Symposium T: materials for solar hydrogen via photo-electrochemical production

Water oxidation catalysis by molecular metal-oxides

Andrea Sartorel^{a,*}, Mauro Carraro^a, Gianfranco Scorrano^a, Marcella Bonchio^b

^a University of Padova, Department of Chemical Sciences, via Marzolo 1 35131 Padova (Italy)

^b Institute on Membrane Technology, CNR, via Marzolo 1 35131 Padova (Italy)

Abstract

Water oxidation catalysis is recognized as the bottleneck for the development of efficient devices based on artificial photosynthesis, that is the light driven water splitting into hydrogen and oxygen. A recent breakthrough in this field, is the development of a molecular, fast and robust water oxidation catalyst namely a fully inorganic tetranuclear ruthenium complex with polyoxometalate ligands. The crystal structure of $[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4(\text{SiW}_{10}\text{O}_{36})_2]^{10-}$, **1**, evidences the entrapment of an adamantane like, tetranuclear ruthenium(IV)-oxo core, by two decatungtosilicate units. Several spectroscopic techniques confirm the maintenance of the structure in aqueous solution. In the presence of Ce(IV) as sacrificial electron acceptor, **1** catalyzes water oxidation to oxygen, showing up to 500 turnovers and a turnover frequency of 0.125 s^{-1} . The synergistic effect of the four ruthenium centres has a fundamental effect on such astounding performance, as confirmed by spectroscopic and computational characterization of five competent intermediates involved in the catalytic cycle, in strict analogy with the natural paradigm of the oxygen evolving centre in Photosystem II. Interestingly, **1** efficiently catalyzes water oxidation in the presence of photogenerated oxidants, as well; this fundamental feature is probably related to very fast hole scavenging of anionic **1** from cationic photogenerated oxidants, such as $\text{Ru}(\text{bpy})_3^{3+}$. Thus, **1** is an ideal candidate for the assembly of high efficient oxygen-evolving anodes into nanostructured devices for artificial photosynthesis.

© 2012 Published by Elsevier Ltd. Selection and/or peer review under responsibility of European Material Research Society (E-MRS)
Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Artificial photosynthesis; water oxidation catalysis; molecular catalysts; polyoxometalates; ruthenium

1. Introduction

Artificial photosynthesis converts sunlight into chemical energy, by performing the splitting of water into hydrogen and oxygen,[1] and can therefore be considered as a promising route to produce renewable fuels, satisfying the ever increasing global energy demand. Nevertheless, the entire process has a formidable complexity, being constituted by the assembly of different components, in a modular approach.[2] These deal with light harvesting, energy transfer, electron transfer and redox catalysis. In particular, the research for redox catalysts

* Corresponding author. Tel.: +39 049 827 5252; fax: +39 049 827 5289.
E-mail address: andrea.sartorel@unipd.it.

enabling water oxidation to oxygen has encountered severe difficulties due to the enormous complexity of this half reaction, which involves the removal of 4 protons and 4 electrons from two water molecules, with the contemporary formation of a new oxygen – oxygen bond. Indeed, the limited development of water oxidation catalysts is nowadays recognized as the bottleneck of the entire water splitting process, although some relevant results have been reported in the last few years.[3] Over the course of billions of years, Nature has developed and refined the Oxygen Evolving Centre (OEC) in Photosystem II to drive the oxidation of water in green plants at minimal energy cost. Crystallographic and spectroscopic studies revealed that the natural OEC is constituted by four manganese and one calcium atoms, connected through μ -oxo and μ -hydroxo bridges;[4-7] the ability of the OEC to catalyze water oxidation stems from its possibility to reach at least five oxidation states (S_i , $i=0-4$), where the manganese core is consecutively oxidized by a radical cation of the chlorophyll, with the contemporary loss of 4 protons.[8] The OEC, in its highest oxidation state S_4 , is then able to oxidize water to oxygen restoring its initial state S_0 , in a single step occurring in the ms timescale.[9] It is worth to mention that the oxidative conditions where the catalysis takes place inflict a lethal damage to the OEC itself, which has to undergo a mechanism of self repairing every 30-60 minutes.[10] Nevertheless, the formidable activity of the OEC (up to 400 cycles per second) has inspired the design and the synthesis of several artificial molecular water oxidation catalysts (WOC) with considerable activity. The first WOC is the ruthenium blue dimer, $[(bpy)_2Ru(H_2O)]\mu-ORu(H_2O)(bpy)_2$ ($bpy = 2,2'$ -bipyridine), that was reported by T.J. Meyer in 1982.[11] Since then, ruthenium complexes have played the major role in water oxidation catalysis, and reviews on the most relevant ones were recently reported by Llobet et al.[12-13] In the last few years, new ruthenium species have been reported to catalyze water oxidation [14-15] although other metals have also been considered, leading to the development of molecular WOC based on Iridium [16] and on more abundant metals such as Manganese,[17] Cobalt [18] and Iron.[19] A serious limit of these molecular WOC is the stability under catalytic regime, since they are mainly constituted by organic ligands, which suffer from oxidative bleaching under the oxidative conditions required to perform water oxidation catalysis.

In this paper we present the results achieved in the development of innovative WOC, based on transition metals stabilized by polyoxometalate (POM) ligands. These are polyanionic oxo-clusters, formed by the condensation of oxo groups and early transition metals in their highest oxidation states, such as W(VI). Being totally inorganic, these molecular metal oxo species display relevant robustness towards oxidative degradation, and are therefore promising ligands to design stable WOC with long lasting performance

2. Polyoxometalates as water oxidation catalysts

2.1 Polyoxometalates. Polyoxometalates (POMs) are molecular, polyanionic, multi-metal oxygen cluster anions, generally assembled from aqueous solutions of early transition metals in their highest oxidation states, depending on specific conditions such as pH and temperature.[20] These species display remarkable functional properties that depend on their elemental composition, structure, and associated counterion, fostering their application in different disciplines.[21] In the specific field of water oxidation catalysis, the adoption of POM based ligands guarantees the design of robust catalysts overcoming the problem of degradation of the ligand scaffold generally observed employing organic ligands, under the aggressive, oxidizing conditions required to perform water oxidation. Relevant examples of POM ligands are reported in figure 1.

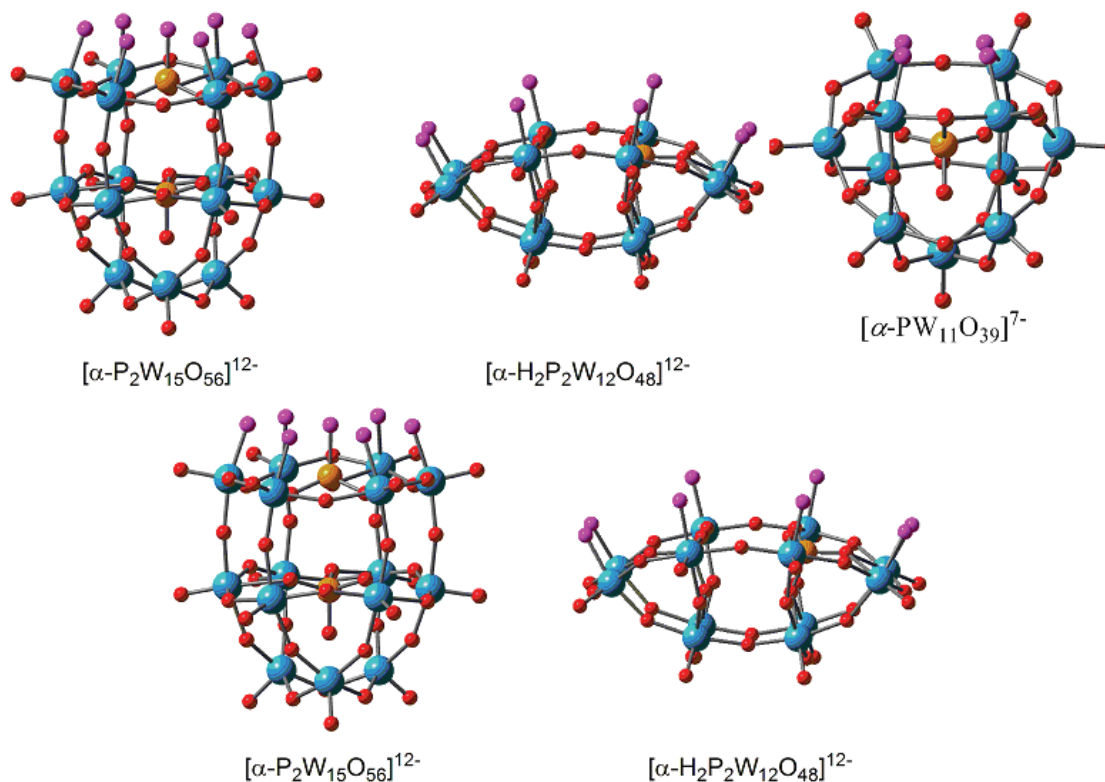


Figure 1. Examples of POM based ligands. Blue atoms: tungsten; grey atoms: silicon; orange atoms: phosphorous; red atoms: oxygen; purple atoms: nucleophilic oxygens of the coordination site. The Greek letters within the formula identify specific structural isomers, for more details see references [20] and [21].

Complexation of several transition metals by POM ligands is usually achieved in aqueous solution, and the resulting complexes show remarkable stability, especially towards oxidizing conditions, since the POM framework is constituted by metals in their highest oxidation states. Moreover, POMs can be conveniently embedded in suitable materials such as polymeric membranes[22] and chitosan nanoparticles,[23] that can further protect them under reaction conditions, while driving their reactivity. Thus, all these features make POMs ideal candidates to design structurally stable, molecular OEC.

2.2 A tetraruthenium polyoxometalate as a molecular WOC. POM ligands were first considered for the design of molecular WOC in 2004 by Howells et al.,[24] who reported electrochemical water oxidation catalyzed by the species $\text{Na}_{14}[\text{Ru}^{\text{III}}_2\text{Zn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$; nevertheless, structural disorder of this species did not allow unambiguous characterization of the actual catalyst, thus hampering mechanistic studies. The first structurally characterized POM based WOC was the tetraruthenium $\{\text{Ru}_4(\mu\text{-OH})_2(\mu\text{-O})_4(\text{H}_2\text{O})_4[\gamma\text{-SiW}_{10}\text{O}_{36}]\}^{10-}$ species, **1**, (structure is shown in figure 2), which is readily prepared in aqueous solution by reaction of the ligand $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$, shown in figure 1, with suitable ruthenium precursors in aqueous solution. This catalyst was reported in 2008 independently by two groups,[25,26] and its structure displays interesting analogies with that of the OEC in Photosystem II, both being constituted by four redox active transition metals connected through $\mu\text{-oxo}$ or $\mu\text{-hydroxo}$ bridges. A further similarity with the OEC is given by the ability of **1** to undergo consecutive one-electron oxidations, coupled with proton removal; these proton coupled electron transfer lead to redox potential levelling, which is recognized as one of the key features to achieve water oxidation at relatively low potentials.[27]

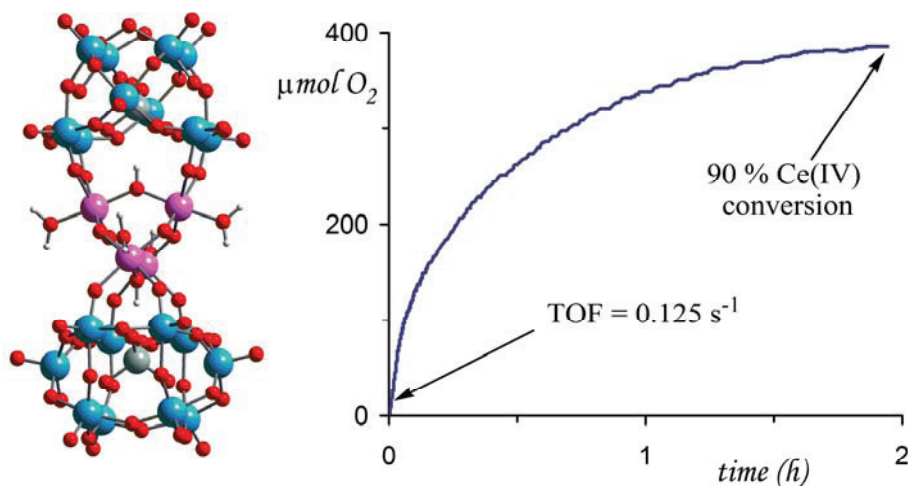
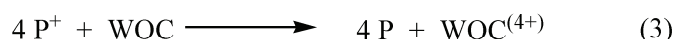
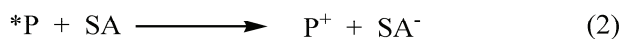


Figure 2. Structure of $\{\text{Ru}_4(\mu\text{-OH})_2(\mu\text{-O})_4(\text{H}_2\text{O})_4[\gamma\text{-SiW}_{10}\text{O}_{36}]\}^{10-}$, **1**, (left), and oxygen evolution profile in the presence of **1** and Ce(IV) as sacrificial electron acceptor (right): 4.3 μmol **1**, 1720 μmol Ce(IV) in 10 ml H₂O at 20°C.[25]

Activity of **1** in water oxidation was initially studied under dark conditions, in the presence of sacrificial electron acceptors such as Ce(IV),[25] or Ru(bpy)₃³⁺. [26] Adding an excess of Ce(IV), vigorous oxygen bubbling is observed from aqueous solutions of **1**, with an initial turnover frequency of 0.125 cycles·s⁻¹. [25] A second and a third recharges of Ce(IV) produce equivalent amounts of evolved oxygen, with **1** cycling up to 500 total turnovers (defined as the number of moles of oxygen per mole of catalyst). Also, the first order dependence of the oxygen evolving rate on the initial concentration of **1** confirms the nature of a molecular species as the actual catalyst and no formation of colloidal RuO₂, which is known to catalyze water oxidation since late seventies of last Century. [28] With Ru(bpy)₃³⁺ as the oxidant, up to 18 turnovers are achieved, with an initial turnover frequency of 0.45-0.60 s⁻¹. [26]

The mechanism of water oxidation catalyzed by **1** is still under investigation, although some insights have been provided by pertinent publications. [29-32] The main difficulty is related to the characterization of the competent intermediates, involved in the catalytic cycle. In addition, isolation of different intermediates was possible only in acidic solution, since the redox waves are pH-dependent, and in neutral environment they collapse into a single one, observed just before the discharge of water. Nevertheless, a general consensus has emerged in the possibility of **1** to undergo several consecutive 1 e⁻ oxidations, coupled with proton removal, that finally lead to an active form of the catalyst, capable of oxidizing water and restoring the resting state of the catalyst itself; isolation of the active form of **1** in water is hampered by its very high activity, leading to concomitant oxygen evolution. Nevertheless, the redox features of **1** and its ability to undergo proton coupled electron transfers leads again to a strict analogy with the behaviour of the OEC in Photosystem II, thus providing an outstanding proof of biomimetic catalysis, employing a totally inorganic species.

2.3 Light driven water oxidation catalyzed by 1. In order to propose a catalyst for applications in artificial photosynthesis, it is important to prove its activity not only under dark conditions, but also in light driven water oxidation, taking advantage of a photosensitizer (P) and a sacrificial electron acceptor (SA). According to scheme 1, light is absorbed by P which is then promoted to its excited state, *P (eq. 1 in scheme 1). *P then releases one electron to the sacrificial acceptor SA, forming the oxidized form of the photosensitizer P⁺ (eq. 2 in scheme 1). P⁺ is then able to drive oxidation of the WOC to its active form WOC⁽⁴⁺⁾, while the contemporary formed P is then ready to restart another cycle (eq. 3 in scheme 1). Finally, WOC⁽⁴⁺⁾ is then able to oxidize water to dioxygen, (eq. 4 in scheme 1).



Scheme 1. General representation of light induced O_2 generation in the presence of a photosensitizer (P), a sacrificial electron acceptor (SA) and a water oxidation catalyst (WOC). Please note that the active form of the WOC is indicated as $WOC^{(4+)}$, since usually four mono electronic oxidation steps are required to generate this species. Nevertheless, the contemporary removal of protons from the WOC may lead to a lower actual charge on $WOC^{(4+)}$.

Within such scheme, several parameters may affect the yield and the efficiency of the process: (i) the ability of P to absorb light; (ii) the life of the excited state $*P$; (iii) the redox potential of the P^+/P couple, which has to be high enough to oxidize the WOC to the active form responsible for oxygen production; (iv) the rates of reaction of $*P$ with SA and of P^+ with the WOC. Indeed, several competing unproductive pathways may occur, leading to decomposition of P and to decreased efficiency of the light driven oxygen production. In the current literature, the most widely explored system uses $Ru(bpy)_3^{2+}$ as the photosensitizer and the persulfate anion, $S_2O_8^{2-}$, as the SA.[33] Using the $Ru(bpy)_3^{2+} / S_2O_8^{2-}$ system, and **1** as the WOC, water oxidation was observed by employing visible light, with the catalyst **1** cycling up to 350 turnovers.[34] One of the reasons for the efficient catalysis by **1** under such conditions, stems from very fast reaction rates between **1** and the oxidized form of the photosensitizer, $Ru(bpy)_3^{3+}$ (hole scavenging, eq. 3 in scheme 1). Indeed, the rate of such reaction was measured by laser flash photolysis experiments and follows a second order kinetic profile, with a rate constant $k = 2.1 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$,[35] that under the reaction conditions implies a μs timescale process (for the sake of comparison, this process usually happens in the ms timescale region by employing IrO_2 nanoparticles as the WOC [36]). This very fast reaction rate, close to the diffusion controlled limit, restricts degradation of the oxidized sensitizer $Ru(bpy)_3^{3+}$, which, in the absence of efficient hole scavenging, undergoes self bleaching upon degradation of the bpy ligands. Presumably, this fast process may be ascribed to the complementary charge of the anionic **1** and the cationic $Ru(bpy)_3^{3+}$.

In order to efficiently exploit solar light in water oxidation processes, it would be highly desirable to use photosensitizers with extended absorption in the visible region. To this aim, multi nuclear ruthenium dendrimers with polypyridine photosensitizers have been extensively investigated in the last few decades.[37]

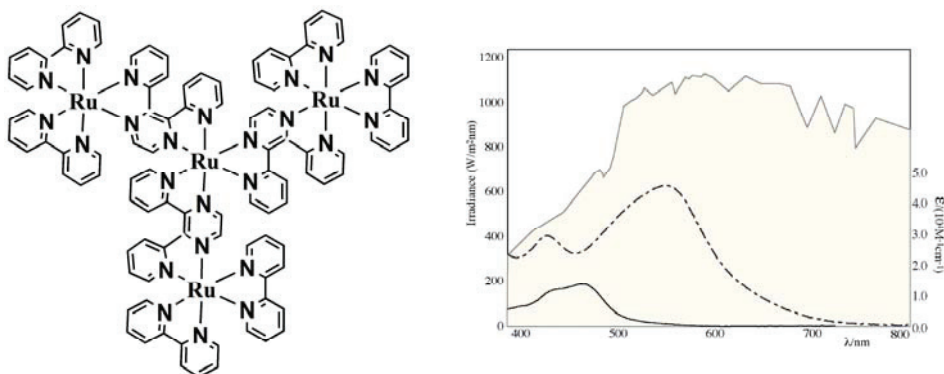


Figure 3. Representation of the structure of $Ru\{(\mu\text{-dpp})Ru(bpy)_2\}_3^{8+}$, **2**, (left) and comparison among solar emission at the sea level (visible region, yellow area), absorption spectra of $Ru(bpy)_3^{2+}$ (solid line) and **2** (dashed-dotted line), (right).

This species, based on the use of 2,3-bis(2'-pyridyl)pyrazine (dpp) as bridging ligand between different metal centres, offer several advantages over $\text{Ru}(\text{bpy})_3^{2+}$, since they display an extended absorption towards the visible part of the spectrum. In particular, the chemical structure and the absorption spectra of the tetraruthenium $\text{Ru}\{(\mu\text{-dpp})\text{Ru}(\text{bpy})_2\}_3^{8+}$ photosensitizer, **2**, are reported in figure 3. Moreover, the first oxidation event of **2** involves the simultaneous one electron oxidation of the four metal centres, and occurs at around 1.70 V vs NHE, while for $\text{Ru}(\text{bpy})_3^{2+}$ is at 1.26 V vs NHE. Therefore, these properties make **2** a very interesting photosensitizer for water oxidation applications.[38] Indeed, combining **2** with $\text{S}_2\text{O}_8^{2-}$ as SA and **1** as the WOC lead to oxygen generation by using visible light ($\lambda > 550$ nm).[39] After three hours of irradiation ($[\mathbf{1}] = 6 \cdot 10^{-5}$ M; $[\mathbf{2}] = 10^{-4}$ M; $[\text{S}_2\text{O}_8^{2-}] = 10^{-2}$ M; phosphate buffer 20 mM at pH 7.2, $\lambda_{\text{irr}} = 550$ nm), persulfate conversion is $> 90\%$ (corresponding to 80 turnovers of **1**), accompanied by minimal decomposition of **2**, estimated from UV-Vis analysis being less than 5%. In photoinduced water oxidation, a relevant parameter to consider is the quantum yield, defined as the number of molecules of produced oxygen divided by the number of photons; when $\text{S}_2\text{O}_8^{2-}$ is used as the sacrificial electron acceptor, the first electron transfer from $^*\text{P}$ to $\text{S}_2\text{O}_8^{2-}$ (eq. 2 in scheme 1) produces P^+ and a radical SO_4^- , and this latter oxidizes a second molecule of P; therefore, two photons are required to produce one molecule of oxygen, and the maximum value achievable for the quantum yield is 0.50. In the **1** / **2** / $\text{S}_2\text{O}_8^{2-}$ system, the experimental value of the quantum yield using 550 nm light is 0.30,[39] significantly larger than the value of 0.045 reported by using $\text{Ru}(\text{bpy})_3^{2+}$ as the photosensitizer (with 450-520 nm light);[34], this means that 60% of the photons are actually used to produce oxygen. This result, together with the possibility of accessing a large fraction of the red portion of visible spectra, up to 700 nm, paves the way towards sustainable hydrogen economy from light driven water splitting.

2.4 Nanostructured Oxygen Evolving Anodes.

In the perspective of integrating **1** in a device for artificial photosynthesis, it is necessary to support it onto an electrode, performing heterogeneous water oxidation catalysis. In such a device, several requirements must be guaranteed, such as high surface area of the support to provide sufficient loading of the catalyst, efficient electron conductivity from the catalyst to the electrode, and robustness of the material to the oxidizing conditions required to perform water oxidation. These requirements were satisfied by anchoring **1** onto a conductive bed of multi-walled carbon nanotubes (**MWCNT**);[40] a chemical modification of the nanotubes offers indeed the possibility to covalently bind pendant dendrimeric chains containing ammonium groups,[41] which in a second step allow the support of anionic **1** by exploiting attractive electrostatic interactions (figure 4). Several spectroscopic and microscopic techniques confirmed loading of **1** onto the surface of the tubes mainly as molecular entities, which is crucial in order to exploit all the redox centres and access single-site catalysis. The hybrid material, **1-MWCNT**, was drop casted onto Indium Tin Oxide (ITO) electrodes, evaluating by electrochemical techniques the activity of the resulting electrode. Indeed, the catalytic wave due to water oxidation was observed by application of an external bias, under dark conditions, at overpotential of ca. 0.35 Volt.[40] Bare ITO alone and ITO doped with multi-wall carbon nanotubes electrodes display instead very high overpotentials, confirming that water oxidation catalysis is carried on by the presence of **1**. The turnover frequency of **1** was calculated to be up to 300 h^{-1} at 0.60 V overpotential. An analogous functionalization with cationic pendant groups was made also on amorphous carbon (**AC**), allowing preparation of the **1-AC** hybrid material; nevertheless, the current observed by casting **1-AC** or **1** alone onto ITO resulted much inferior with respect to the one observed with **1-MWCNT**, highlighting the important role of the tubes, especially related to the conductivity features of the resulting material (figure 4). Moreover, the current due to water oxidation was observed under consecutive voltammetric scans, indicating a good stability of the electrode. Recently, support of the catalyst **1** and activity of the resulting hybrid material has been achieved also by non covalent functionalization of nanotubes with cationic moieties, thus widening the synthetic procedures for the preparation of efficient anodes working at mild overpotential.[42]

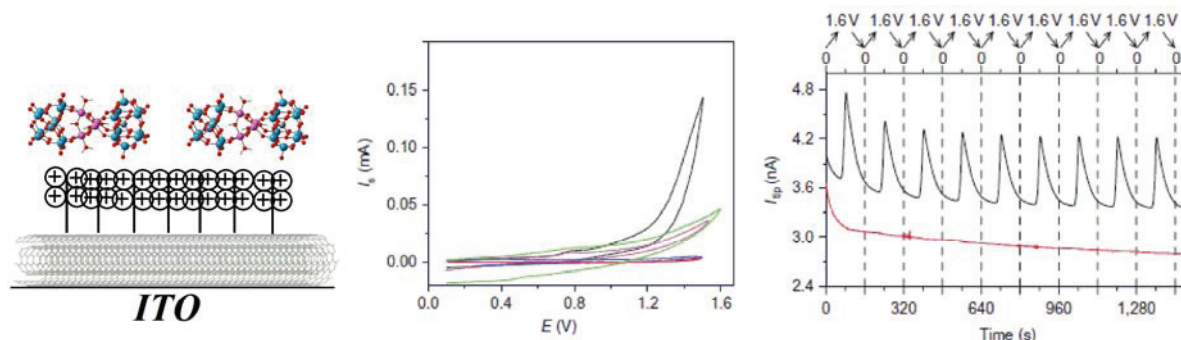


Figure 4. Representation of the electrode from deposition of the **1-MWCNT** hybrid material onto ITO (left). Cyclic voltammetry curves of electrodes drop casted with different materials: black curve: **1-MWCNT**, green curve: **1-AC**, purple curve: **1** alone, blue curve: **MWCNT**, red curve: bare ITO (centre). Current transients observed after nine sequential scans applied to the ITO electrode with **1-MWCNT** (right). Adapted from [42].

3. Conclusions and Perspectives

The development of molecular water oxidation catalysts is a subject of current interest in the pursuit of solar light exploitation for production of renewable fuels. A recent breakthrough in this field is the development of transition metal species with totally inorganic polyoxometalate ligands. In particular, the $\{\text{Ru}_4(\mu\text{-OH})_2(\mu\text{-O})_4(\text{H}_2\text{O})_4[\gamma\text{-SiW}_{10}\text{O}_{36}]\}^{10-}$ (**1**) provides:

- (i) high activity in water oxidation catalysis, due to the synergistic action of four redox active metals, in analogy with the natural OEC in Photosystem II;
- (ii) remarkable robustness under catalytic conditions, by taking advantage of the inorganic W(VI) cage of the POM ligands;
- (iii) efficient interaction with ruthenium polypyridine photosensitizers, allowing light driven water oxidation with unprecedented quantum yields;
- (iv) possibility of support onto a conductive bed of multi walled carbon nanotubes, for the design of nanostructured oxygen evolving anodes.

An important step forward in this field, would be the replacement of rare ruthenium with more abundant materials, namely first row transition metals. Recently, a tetracobalt POM based species, $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$, was reported to be an actual WOC, under dark [43] and illuminated conditions.[44] Activity of this catalyst is remarkable, with claimed turnover frequencies up to $8 \text{ cycles}\cdot\text{s}^{-1}$ under dark conditions[43] and a quantum yield of 0.15 using the $\text{light}/\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ system;[44] nevertheless, water oxidation by such a species was studied in slightly basic conditions ($\text{pH} = 8$), while the optimal work conditions would be neutral water.

4. Acknowledgements

We gratefully thank Prof. Franco Scandola and Dr. Michele Orlandi (University of Ferrara, Italy), Prof. Sebastiano Campagna, Dr. Fausto Puntoriero and Giuseppina La Ganga (University of Messina, Italy) and Prof. Maurizio Prato and Dr. Francesca M. Toma (University of Trieste, Italy) for their great contributions on several aspects of this work.

Financial support from the University of Padova (Progetto Strategico 2008, HELIOS and Progetto di Ricerca di Ateneo, PRAT CPDA104105/10) and from Fondazione Cariparo (Progetti di Eccellenza 2010, Nano-Mode) is gratefully acknowledged.

5. References

- [1] Wenjing Song, Zuofeng Chen, M. Kyle Brennaman, Javier J. Concepcion, Antonio Otavio T. Patrocinio, Neyde Y. Murakami Iha, Thomas J. Meyer. Making solar fuels by artificial photosynthesis. *Pure and Applied Chemistry* 2011, 83, 749-768.
- [2] James H. Alstrum-Acevedo, M. Kyle Brennaman, Thomas J. Meyer. Chemical approaches to artificial photosynthesis 2. *Inorg. Chem.* 2005, 44, 6802-6827.
- [3] Matthew W. Kanan, Daniel G. Nocera. In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+} . *Science* 2008, 321, 1072-1075.
- [4] Kristina N. Ferreira, Tina M. Iverson, Karim Maghlaoui, James Barber, So Iwata. Architecture of the photosynthetic oxygen-evolving center. *Science* 2004, 303, 1831-1838.
- [5] Bernhard Loll, Jan Kern, Wolfram Saenger, Athina Zouni, Jacek Biesiadka. Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II. *Nature* 2005, 438, 1040-1044.
- [6] Junko Yano, Jan Kern, Kenneth Sauer, Matthew J. Latimer, Yulia Pushkar, Jacek Biesiadka, Bernhard Loll, Wolfram Saenger, Johannes Messinger, Athina Zouni, Vittal K. Yachandra. Where water is oxidized to dioxygen: structure of the photosynthetic Mn_4Ca cluster. *Science* 2006, 314, 821-825.
- [7] Yasufumi Umena, Keisuke Kawakami, Jian-Ren Shen, Nobuo Kamiya. Crystal structure of oxygen evolving photosystem II at a resolution of 1.9 Å. *Nature* 2011, 473, 55-60.
- [8] Bessel Kok, Bliss Forbush, Marion McGloin. Cooperation of charges in photosynthetic O_2 evolution-I, a linear four step mechanism. *Photochem. Photobiol.* 1970, 11, 457-475.
- [9] James P. McEvoy, Gary W. Brudvig. Water-splitting chemistry of photosystem II. *Chem. Rev.* 2006, 106, 4455-4483.
- [10] Gennady Ananyev, G. Charles Dismukes. How fast can photosystem II split water? Kinetic performance at high and low frequencies. *Photosynth. Res.* 2005, 84, 355-365.
- [11] Susan W. Gersten, George J. Samuels, Thomas J. Meyer. Catalytic oxidation of water by an oxo-bridged ruthenium dimer. *J. Am. Chem. Soc.* 1982, 104, 4029-4030.
- [12] Isabel Romero, Montserrat Rodríguez, Cristina Sens, Joaquim Mola, Mohan Rao Kollipara, Laia Francàs, Elena Mas-Marza, Lluís Escriche, Antoni Llobet. Ru complexes that can catalytically oxidize water to molecular oxygen. *Inorg. Chem.* 2008, 47, 1824-1834.
- [13] Xavier Sala, Isabel Romero, Montserrat Rodríguez, Lluís Escriche, Antoni Llobet. Molecular catalysts that oxidize water to dioxygen. *Angew. Chem. Int. Ed.* 2009, 48, 2842-2852.
- [14] Yunhua Xu, Andreas Fisher, Lele Duan, Lianpeng Tong, Erik Gabrielsson, Björn Åkermark, Licheng Sun. Chemical and light-driven oxidation of water catalyzed by an efficient dinuclear ruthenium complex. *Angew. Chem. Int. Ed.* 2010, 49, 8934-8937.
- [15] Zuofeng Chen, Javier J Concepcion, Thomas J. Meyer. Rapid catalytic water oxidation by single site, Ru carbene catalyst. *Dalton Trans.* 2011, 40, 3789-3792.
- [16] Neal D. McDaniel, Frederick J. Coughlin, Leonard L. Tinker, Stefan Bernhard. Cyclometalated iridium(III) aquo complexes: efficient and tunable catalysts for the homogeneous oxidation of water. *J. Am. Chem. Soc.* 2008, 130, 210-217.
- [17] Robin Brimblecome, Gerhard F. Swiegers, G. Charles Dismukes, Leone Spiccia. Sustained water oxidation photocatalysis by a bioinspired manganese cluster. *Angew. Chem. Int. Ed.* 2008, 47, 7335-7338.
- [18] Giuseppina La Ganga, Fausto Puntoriero, Sebastiano Campagna, Irene Bazzan, Serena Berardi, Marcella Bonchio, Andrea Sartorel, Mirco Natali, Franco Scandola. Light-driven water oxidation with a molecular tetra-cobalt(III) cubane cluster. *Faraday discussions*, accepted for publication, Manuscript ID: FD-ART-05-2011-000093.

- [19] W. Chadwick Ellis, Neal D. McDaniel, Stefan Bernhard, Terrence J. Collins. Fast water oxidation using iron. *J. Am. Chem. Soc.* 2010, 132, 10990-10991.
- [20] Michael T. Pope, Achim Müller. Polyoxometalate chemistry – an old field with new dimensions in several disciplines. *Angew. Chem. Int. Ed.* 1991, 30, 34-48.
- [21] De-Liang Long, Eric Burkholder, Leroy Cronin. Polyoxometalate clusters, nanostructures and materials: from self assembly to designer materials and devices. *Chem. Soc. Rev.* 2007, 36, 105-121.
- [22] Mauro Carraro, Martino Gardan, Gianfranco Scorrano, Enrico Drioli, Enrica Fontananova, Marcella Bonchio. Solvent-free, heterogeneous photooxygenation of hydrocarbons by Hyflon® membranes embedding a fluorine-tagged decatungstate. *Chem. Commun.* 2006, 4533-4535.
- [23] Georg Geisberger, Susann Paulus, Mauro Carraro, Marcella Bonchio, Greta R. Patzke. Synthesis, characterisation and cytotoxicity of polyoxometalate/carboxymethyl chitosan nanocomposites. *Chemistry a Eur. J.* 2011, 17, 4619-4625.
- [24] Annette R. Howells, Anand Sankarraj, Curtis Shannon. A diruthenium-substituted polyoxometalate as an electrocatalyst for oxygen generation. *J. Am. Chem. Soc.* 2004, 126, 12258-12259.
- [25] Andrea Sartorel, Mauro Carraro, Gianfranco Scorrano, Rita De Zorzi, Silvano Geremia, Neal D. McDaniel, Stefan Bernhard, Marcella Bonchio. Polyoxometalate embedding of a tetraruthenium(IV)-oxo-core by template-directed metalation of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$: a totally inorganic oxygen-evolving catalyst. *J. Am. Chem. Soc.* 2008, 130, 5006-5007.
- [26] Yurii V. Geletii, Bogdan Botar, Paul Kögerler, Daniel A. Hillesheim, Djamaladdin G. Musaev, Craig L. Hill. An all-inorganic, stable, and highly active tetraruthenium homogeneous catalyst for water oxidation. *Angew. Chem. Int. Ed.* 2008, 47, 3896-3899.
- [27] Feng Liu, Javier J. Concepcion, Jonah W. Jurss, Thomas Cardolaccia, Joseph L. Templeton, Thomas J. Meyer. Mechanism of water oxidation from the blue dimer to photosystem II. *Inorg. Chem.* 2008, 47, 1727-1752.
- [28] John Kiwi, Michael Grätzel. Ruthenium oxide, a suitable redox catalyst to mediate oxygen production from water. *Chimia* 1979, 33, 289-291.
- [29] Andrea Sartorel, Pere Miró, Enrico Salvadori, Sophie Romain, Mauro Carraro, Gianfranco Scorrano, Marilena Di Valentin, Antoni Lobet, Carles Bo, Marcella Bonchio. 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, 16051-16053.
- [30] Andrea Sartorel, Melissa Truccolo, Serena Berardi, Martino Gardan, Mauro Carraro, Francesca Maria Toma, Gianfranco Scorrano, Maurizio Prato, Marcella Bonchio. Oxygenic polyoxometalates: a new class of molecular propellers. *Chem. Commun.* 2011, 47, 1716-1718.
- [31] Yurii V. Geletii, Claire Besson, Yu Hou, Qiushi Yin, Djamaladdin G. Musaev, David Quiñero, Rui Cao, Kenneth I. Hardcastle, Anna Proust, Paul Kögerler, Craig L. Hill. Structural, physicochemical, and reactivity properties of an all-inorganic, highly active tetraruthenium homogeneous catalyst for water oxidation. *J. Am. Chem. Soc.* 2009, 131, 17360-17370.
- [32] David Quiñero, Alexey L. Kaledin, Aleksey E. Kuznetsov, Yurii V. Geletii, Claire Besson, Craig L. Hill, Djamaladdin G. Musaev. Computational studies of the geometry and electronic structure of an all-inorganic and homogeneous tetra-Ru-polyoxotungstate catalyst for water oxidation and its four subsequent one-electron oxidized forms. *J. Phys. Chem. A* 2010, 114, 535-542.
- [33] Henry S. White, William G. Becker, Allen J. Bard. Photochemistry of the tris(2,2'-bipyridine)ruthenium(II)-peroxydisulfate system in aqueous and mixed acetonitrile-water solutions. Evidence for a long-lived photoexcited ion pair. *J. Phys. Chem.* 1984, 88, 1840-1846.
- [34] Yurii V. Geletii, Zhuangqun Huang, Yu Hou, Djamaladdin G. Musaev, Tianquan Lian, Craig L. Hill. Homogeneous light-driven water oxidation catalyzed by a tetraruthenium complex with all inorganic ligands. *J. Am. Chem. Soc.* 2009, 131, 7522-7523.
- [35] Michele Orlandi, Roberto Argazzi, Andrea Sartorel, Mauro Carraro, Gianfranco Scorrano, Marcella Bonchio, Franco Scandola. Ruthenium polyoxometalate water splitting catalyst: very fast hole scavenging from photogenerated oxidants. *Chem. Commun.* 2010, 46, 3152-3154.
- [36] W. Justin Youngblood, Seung-Hyun Anna Lee, Yoji Kobayashi, Emil A. Hernandez-Pagan, Paul G. Hoertz, Thomas A. Moore, Ana L. Moore, Devens Gust, Thomas E. Mallouk. Photoassisted overall water splitting in a visible light-absorbing dye-sensitized photoelectrochemical cell. *J Am Chem Soc* 2009, 131, 926-927.

[37] Fausto Puntoriero, Andrea Sartorel, Michele Orlandi, Giuseppina La Ganga, Scolastica Serroni, Marcella Bonchio, Franco Scandola, Sebastiano Campagna. Photoinduced water oxidation using dendrimeric Ru(II) complexes as photosensitizers. *Coord. Chem. Rev.* 2011, in press, DOI: 10.1016/j.ccr.2011.01.026.

[38] Giuseppina La Ganga, Francesco Nastasi, Sebastiano Campagna, Fausto Puntoriero. Photoinduced water oxidation sensitized by a tetranuclear Ru(II) dendrimer. *Dalton Trans.* 2009, 9997-9999.

[39] Fausto Puntoriero, Giuseppina La Ganga, Andrea Sartorel, Mauro Carraro, Gianfranco Scorrano, Marcella Bonchio, Sebastiano Campagna. Photo-induced water oxidation with a tetra-nuclear ruthenium sensitizer and catalyst: a unique 4×4 ruthenium interplay triggering high efficiency with low-energy visible light. *Chem. Commun.* 2010, 46, 4725-4727.

[40] Francesca M. Toma, Andrea Sartorel, Matteo Iurlo, Mauro Carraro, Pietro Parisse, Chiara Maccato, Stefania Rapino, Benito R. Gonzalez, Heinz Amenitsch, Tatiana Da Ros, Loredana Casalis, Andrea Goldoni, Massimo Marcaccio, Gianfranco Scorrano, Giacinto Scoles, Francesco Paolucci, Maurizio Prato, Marcella Bonchio. Efficient water oxidation at carbon nanotube-polyoxometalate electrocatalytic interfaces. *Nature Chem.* 2010, 2, 826-831.

[41] M. Antonia Herrero, Francesca M. Toma, Khuloud T. Al-Jamal, Kostas Kolesteros, Alberto Bianco, Tatiana Da Ros, Fouzia Bano, Loredana Casalis, Giacinto Scoles, Maurizio Prato. Synthesis and characterization of a carbon nanotube-dendron series for efficient siRNA delivery. *J. Am. Chem. Soc.* 2009, 131, 9843-9848.

[42] Francesca M. Toma, Andrea Sartorel, Matteo Iurlo, Mauro Carraro, Stefania Rapino, Lena Hooper-Burkhardt, Tatiana Da Ros, Massimo Marcaccio, Gianfranco Scorrano, Francesco Paolucci, Marcella Bonchio, Maurizio Prato. Tailored functionalization of carbon nanotubes for electrocatalytic water splitting and sustainable energy applications. *ChemSusChem*, 2011 in press, DOI: cssc.201100089.

[43] Qiushi Yin, Jeffrey Miles Tan, Claire Besson, Yurii V. Geletii, Djameladdin G. Musaev, Aleksey E. Kuznetsov, Zhen Luo, Ken I. Hardcastle, Craig L. Hill. A fast soluble carbon-free molecular water oxidation catalyst based on abundant metals. *Science* 2010, 328, 342-345.

[44] Zhuangqun Huang, Zhen Luo, Yurii V. Geletii, James W. Vickers, Qiushi Yin, David Wu, Yu Hou, Yong Ding, Jie Song, Djameladdin G. Musaev, Craig L. Hill, Tianquan Lian. Efficient light-driven carbon-free cobalt based molecular catalyst for water oxidation. *J. Am. Chem. Soc.* 2011, 133, 2068-2071.