Kinetics and mechanisms of catalytic water oxidation

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The kinetics and mechanisms of thermal and photochemical oxidation of water with homogeneous and heterogeneous catalysts, including conversion from homogeneous to heterogeneous catalysts in the course of water oxidation, are discussed in this review article. Molecular and homogeneous catalysts have the advantage to clarify the catalytic mechanisms by detecting active intermediates in catalytic water oxidation. On the other hand, heterogeneous nanoparticle catalysts have advantages for practical applications due to high catalytic activity, robustness and easier separation of catalysts by filtration as compared with molecular homogeneous precursors. Ligand oxidation of homogeneous catalysts sometimes results in the dissociation of ligands to form nanoparticles, which act as much more efficient catalysts for water oxidation. Since it is quite difficult to identify active intermediates on the heterogeneous catalyst surface, the mechanism of water oxidation has hardly been clarified under heterogeneous catalytic conditions. This review focuses on the kinetics and mechanisms of catalytic water oxidation with homogeneous catalysts, which may be converted to heterogeneous nanoparticle catalysts depending on various reaction conditions.

1. Introduction

Clean and sustainable energy production using solar energy has become more and more important as the world energy demand increases due to population growth and global industrialisation.1–7 Extensive efforts have been made to produce solar fuels as an artificial version of photosynthesis.7–26 Artificial photosynthesis consists of light
harvesting and charge-separation processes together with catalytic processes for the oxidation of water to evolve O₂ and the reduction of water to evolve H₂, which can be combined with CO₂ fixation. Photoinduced energy transfer and charge-separation (CS) processes in the photosynthetic reaction centres in Photosystem I (PSI) and Photosystem II (PSII) have been well mimicked and many model compounds have been synthesized to study the photodynamics extensively. With regard to the hydrogen evolution reaction (HER), various metal nanoparticles (MNPs) have been used as efficient HER catalysts. Homogeneous catalysts have also been developed for CO₂ fixation by H₂ under normal pressure of H₂ and CO₂ at ambient temperature. The most difficult part to be further developed in the artificial version of natural photosynthesis is the catalytic water oxidation reaction (WOR) to release four electrons and four protons to evolve O₂. In natural photosynthesis, the water oxidation catalyst (WOC) consists of a manganese-oxo-calcium cluster (Mn₄CaO₅) in the oxygen evolving complex (OEC) in PSI.

Both molecular (homogeneous) and solid-state (heterogeneous) catalysts have been employed for chemical, electrocatalytic and photocatalytic oxidation of water. In the case of homogeneous WOC, reactive intermediates such as high-valent metal-oxo species are detected during the WOR and the kinetic analysis of the catalytic WOR provides new insights into the rate-determining step (r.d.s.) and the catalytic mechanism. However, there is a critical issue to be clarified, that is, whether metal complexes supported by organic ligands act as molecular and homogeneous catalysts or as precursors of nanoparticle catalysts formed in the course of the WOR acting as much more reactive heterogeneous WOC. In order to identify true WOCs, much caution should be exercised to analyse time profiles and kinetic order and to detect reactive intermediates for homogeneous metal complexes when these could be converted to more active metal oxide NPs in the course of the WORs. Thus, this review focuses on the kinetics and mechanisms of WORs with homogeneous catalysts including the conversion of molecular homogeneous catalysts to metal oxide or hydroxide NPs that act as truly active heterogeneous catalysts in the oxygen evolution reaction (OER), providing insights into the development of much more efficient and robust WOCs.

2. Ruthenium complexes as WOCs

A dinuclear Ru(n) complex \([\text{bpy}]_2(\text{H}_2\text{O})\text{RuORu}(\text{H}_2\text{O})_2(\text{bpy})_2]^+\) (bpy = 2,2’-bipyridine), which is known as a blue dimer, was reported earlier as a homogeneous WOC by Meyer and co-workers in 1982. Since then, a number of ruthenium complexes have been studied extensively as efficient and stable homogeneous WOCs. Mononuclear Ru(n) complexes as well as dinuclear Ru(n) complexes act as homogeneous WOCs. However, dinuclear Ru(n)-bpp complexes (bpp = 3,5-bis(pyridyl)pyrazolate) were reported to decompose in the course of the OER when the bpp ligands were oxidised to evolve CO₂. The catalytic WOR activity was decreased by the ligand oxidation of mononuclear Ru(n) complexes with organic ligands. In order to enhance the stability of Ru complexes during the OER, non-oxidisable inorganic ligands such as polyoxometalates (POMs) were employed instead of oxidisable organic ligands. For example, a tetrarnuclear ruthenium polyoxometalate complex (Ru₄POM) was reported to act as an effective WOC with a turnover number (TON = 23) based on a ruthenium centre. Mononuclear ruthenium complexes bearing Keggin-type lacunary heteropolytungstate, \([\text{Ru}^{III}(\text{H}_2\text{O})\text{SiW}_{11}\text{O}_{39}]^{5−}\) (1) and \([\text{Ru}^{II}(\text{H}_2\text{O})\text{GeW}_{11}\text{O}_{39}]^{5−}\) (2) (Fig. 1), were also reported to act as efficient and robust homogeneous catalysts for the WOR by (NH₄)₂[CeIV(NO₃)₆] (CAN). Although CAN is not an environmentally benign oxidant, CAN is useful for the mechanistic study. The oxygen atoms in the evolved O₂ were confirmed to originate from H₂O by carrying out isotope-labelling experiments using H₂¹⁸O.

Cyclic voltammograms of 1 and 2 exhibited three one-electron oxidation processes, all of which are chemically reversible. Based on the pH dependence of the redox couples (Pourbaix diagrams), all the species at the different redox potentials and pH values can be identified (see
Fig. 2. \(^{155}\) The Ru\(^{IV}\)-OH\(_2\) complex is formed at pH 1.0 at an applied potential between 0.62 and 0.90 V (vs. SCE) with no proton loss when the \(E_{1/2}\) value is the same as with the change in pH of around 1.0 (Fig. 2). \(^{155}\) In contrast, the Ru\(^{IV}\)-OH\(_2\) complex is further oxidised to the Ru\(^{V}\)=O complex at pH 1.0 at an applied potential higher than 0.90 V with loss of two protons. The \(E_{1/2}\) value decreases with increasing pH (>1.0) with a slope = 118 mV per pH, which indicates the 1e\(^{-}\)/2H\(^{+}\) process between pH 0 and 2. \(^{155}\) Thus, at pH 1.0, 1 and 2 are oxidised by two equivalents of CAN (\(E_{1/2}\) vs. SCE = 1.21 V) to produce \([\text{Ru}^{V}(\text{O})\text{SiW}_{11}\text{O}_{39}]^{5-}\) and \([\text{Ru}^{V}(\text{O})\text{GeW}_{11}\text{O}_{39}]^{5-}\), respectively. \(^{155}\)

The formation of the Ru\(^{IV}\)-OH\(_2\) and Ru\(^{V}\)=O species by stepwise oxidation of 1 by CAN was indicated by the corresponding stepwise absorption spectral change showing different isobestic points for each step. \(^{155}\) The formation of the Ru\(^{V}\)=O complexes produced in the reactions of 1 and 2 with two equivalents of CAN was confirmed by resonance Raman (rR) and electron paramagnetic resonance (EPR) measurements. \(^{155}\)

The decay rates of CAN by the reactions with 1 and 2 obeyed the first-order kinetics with respect to the initial concentrations of the catalysts 1 and 2. \(^{155}\) If two Ru\(^{VI}\)=O molecules are required for O=O bond formation in the OER, the rate would exhibit parabolic dependence with respect to the catalyst concentration (vide infra). Thus, the r.d.s. may be the nucleophilic attack of H\(_2\)O on the Ru\(^{VI}\)=O complex for the O=O bond formation to produce the Ru\(^{III}\)=OOH species (Scheme 1) \(^{155}\) as reported for other Ru WOCs. \(^{156-158}\) According to Scheme 1, the rate of disappearance of Ce\(^{IV}\) (CAN) is given by eqn (1),

\[
-d[\text{Ce}^{IV}]/dt = k_N k_{cat}[\text{Ru}][\text{H}_2\text{O}]/(k_{-N}[\text{H}^+] + k_{cat}[\text{Ce}^{IV}])
\]

where \(k_N\) is the rate constant of the nucleophilic attack of H\(_2\)O on the Ru\(^{VI}\)=O complex, \(k_{cat}\) is the rate constant of electron transfer (ET) from the Ru\(^{III}\)=OOH complex to Ce\(^{IV}\), and \(k_{-N}\) is the rate constant of the back reaction from the Ru\(^{III}\)=OOH complex with H\(^{+}\) to regenerate the Ru\(^{VI}\)=O complex. \(^{155}\) Eqn (1) agrees with the observed first-order dependence of the WOR rate on the concentration of the catalyst and the saturation dependence of the WOR on the pH and concentration of CAN. \(^{155}\) The decay rate of CAN with 2 in the WOR was 1.5 times faster than that with 1, \(^{157}\) because of the electron-withdrawing effect of germanium, which is reflected in the smaller pK\(_a\) value of 2 than that of 1. \(^{155}\) The kinetic study (vide supra) clarifies the rate-determining step in the catalytic cycle in Scheme 1. However, the reaction intermediates proposed in Scheme 1 after the rate-determining step cannot be detected because of the much faster reactions after the rate-determining step. It is better to start the catalytic cycle from postulated intermediates to support the catalytic mechanism.

A seven-coordinate Ru\(^{V}\)=O intermediate of [Ru(bda)(isq)\(_2\)]\(^{3+}\) (3: bda = 2,2'-bipyridine-6,6'-dicarboxylate, isq = isoquinoline) produced during the WOR was characterised by in situ extended X-ray absorption fine structure analysis, which indicated a Ru=O bond distance of 1.75 ± 0.02 Å, as predicted by DFT calculations (Fig. 3). \(^{159}\) The introduction of methoxy group (–OMe) to isq ligand resulted in a lower activation energy to achieve a high TOF of 1270 s\(^{-1}\) for [Ru(bda)(6-OMe-isq)\(_2\)]\(^{3+}\) (30 μM) in the catalytic WOR by CAN (0.365 M). \(^{160}\) The rate of consumption of CAN electron-donating substituents in [Ru(bda)(6-X-isq)\(_2\)] (X = H, F, Cl, Br and OMe) enhanced the non-covalent interactions between the axial ligands for the bimolecular O–O coupling exhibited a second-order
dependence on catalyst concentration [eqn (2)] at low concentrations of the Ru catalyst. Such a

\[-d(Ce^V)/dt = k_{cat}[Ru]^2\]  \hspace{1cm} (2)

second-order dependence of the WOR rate on the concentration of the Ru catalyst suggests that the bimolecular radical coupling of two RuV\(_\mathrm{O}\) molecules for the O–O bond formation is the r.d.s., as proposed by Llobet, Sun and their co-workers (Scheme 2).\(^\text{161-163}\)

At higher concentrations of the Ru catalyst, the rate law was changed to the first order with respect to the catalyst concentration.\(^\text{166,164}\) This indicates that the r.d.s. is changed from the bimolecular radical coupling of two RuV\(_\mathrm{O}\) molecules to the subsequent mononuclear reaction step.\(^\text{160}\) In such a case, the steady-state catalyst oxidation state during the WOR may be changed from Ru\(^\text{V-O}\) to Ru\(^\text{IV-O-O-RuIV}\) depending on the catalyst concentration. However, such a change of the oxidation state of the Ru catalyst under the steady-state conditions is yet to be clarified.

A seven-coordinate Ru\(^\text{V-O}\) intermediate, [Ru\(^\text{V}(\text{ttaa-N}_3\text{O})\)(py)\(_2\)]\(^+\) (Fig. 4A), was reported to react with H\(_2\)O to produce [Ru\(^\text{III}(\text{OH})(\text{Htda-N}_3\text{O})\)(py)\(_2\)]\(^+\) via the intramolecular proton transfer to the dangling carboxylate (Fig. 4B), which was further oxidised to evolve O\(_2\).\(^\text{158}\) Such an intramolecular proton transfer resulted in much enhancement of the catalytic activity of 4 as indicated by TOF up to 8000 s\(^{-1}\) at pH 7.0 and 50 000 s\(^{-1}\) at pH 10, determined by the foot-of-the-wave analysis of cyclic voltammograms, as compared with TOFs of the related complex ([Ru(bda)(Pic)\(_2\)]) without the dangling carboxylate (TOF = 6 s\(^{-1}\) at pH 7.0 and 14 000 s\(^{-1}\) at pH 12.2).\(^\text{158}\) A Ru\(^\text{V-O}(\text{ttaa-N}_3\text{O})(\text{py})_2\) complex (ttaa = 2,5-bis(6-carboxylatopyridin-2-yl)pyrrol-1-ide) also acts as a very efficient WOC, reaching a TOF\(_\text{MAX}\) value of 9400 s\(^{-1}\) at pH 7.0, which is among the highest ever reported at pH 7.0.\(^\text{165}\)

There has been no report on the conversion of homogeneous ruthenium complexes to heterogeneous nanoparticle catalysts in the OER with CAN. However, ruthenium oxide (RuO\(_2\)) NPs are among the most active WOCs reported so far.\(^\text{166-169}\) Whether Ru complexes with organic ligands are converted to RuO\(_2\) NPs during the WORs should be checked with much caution by using various techniques (vide infra).

3. Metal complex precursors to metal nanoparticle WOCs

3.1. Iridium complexes

Not only ruthenium oxides but also iridium oxides are efficient homogeneous WOCs.\(^\text{170-174}\) Molecular iridium complexes were reported to act as homogeneous WOCs.\(^\text{175-184}\) However, the Cp\(^*\) ligand of [Cp\(^*\)Ir(H\(_2\)O]\(_2\)\]\([\text{SO}_4]\) and [(Cp\(^*\)Ir(OH)]\([\text{OH}]\) (Cp\(^*\) = pentamethylcyclopentadienyl) was oxidised electrochemically to produce an amorphous iridium oxide (IrO\(_x\)) layer containing a carbon admixture deposited onto the anode, which acted as a more active and robust WOC for the electrochemical WOR.\(^\text{185-189}\) Such a change from molecular Ir complexes to IrO\(_x\) NPs as true WOCs was also observed in the catalytic WOR by CAN (vide infra).\(^\text{190,191}\)

The time courses of the rate of WOR by CAN with Ir(\text{III}) complexes, [Ir\(^\text{III}(\text{Cp})\_2(\text{4,4’-R}_2\_2,2’-\text{bpy})\_2\](\text{H}_2\text{O})\]([\text{SO}_4])\] (R = OH (5), OMe (6), Me (7) and COOH (8)) (Fig. 5) in the presence of HNO\(_3\) (0.10 M) in H\(_2\)O are shown in Fig. 6a, where the turnover frequency (TOF) is plotted against the reaction time.\(^\text{191}\) The TOF was determined from the initial decay rate of CAN divided by four \((-d(Ce^V)/dt)/4\) according to the stoichiometry of the WOR by Ce\(^\text{IV}\) (CAN) [eqn (3)]. The TOF of the WOR with 6-8 decreased with the reaction time, whereas the TOF with 5...
increased with time to reach a highest value at 900 s. After the maximum value, the TOF decreased as the CAN was consumed at 1100 s. It was confirmed that the evolved O2 originates from H2O by performing isotope-labelling experiments using H218O. The observed increase in TOF with the reaction time indicates that 5 acts as a precursor for the more reactive catalyst for the WOR by CAN. After all CAN molecules were consumed in the WOR in the 1st cycle, addition of another batch of CAN to the resulting solution started the 2nd cycle. The TOF value at the beginning of the 2nd cycle was virtually the same as the largest value in the 1st cycle as shown in Fig. 6b, where the catalytic activity also remained the same in the 3rd cycle. This indicates that 5 was converted to the active and robust catalyst during the 1st cycle of the WOR.

\[
2\text{H}_2\text{O} + 4\text{Ce}^{IV} \xrightarrow{\text{cat}} \text{O}_2 + 4\text{H}^+ + 4\text{Ce}^{III}
\]  

Dynamic light scattering (DLS) measurements were performed to confirm the formation of NPs during the catalytic WOR by CAN with 5 as shown in Fig. 7, where the size of NPs increased with increasing concentration of the precursor 5. The size of NPs was in the rage of 100–300 nm, as shown by the transmission electron microscopy (TEM) images in Fig. 8. X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique and the XPS spectra of NPs formed in the catalytic WOR by CAN with 5 (Fig. 9) indicate that the Ir 4f7/2 peak of the NPs appeared at 62.8 eV shifted by −0.9 eV in reference to the Ir 4f7/2 peak of IrO2 NPs. The peak of oxygen 1s of the NPs (532.3 eV) also shifted to higher values than that of the reference IrO2 NPs (530.2 eV). Such a shift of the oxygen 1s peak suggests the formation of iridium hydroxide species (Ir(OH)x)3. Thermogravimetry/differential thermal analysis (TG/DTA) measurements also supported the formation of Ir(OH)3 from 5 because the weight loss corresponded to the thermal dehydroxylation reaction from Ir(OH)x to IrO2. Thus, NPs derived from 5 after the catalytic WOR by CAN consist of Ir(OH)x (x = 3) and carbonaceous residues.

The facile conversion of 5 to Ir(OH)x NPs in the catalytic WOR by CAN as compared with 6–8 suggests that the ligand of...
5 was much easily oxidised by CAN than those of 6–8. In fact, the [4,4-(OH)_{2}-bpy] ligand of 5 showed higher reactivity in oxidation by CAN to produce CO_{2} as compared with the ligands of 6–8.\textsuperscript{191}

Organometallic iridium complexes (9–14) in Fig. 10 were also converted to NPs, which act as true catalysts during the catalytic WOR by CAN.\textsuperscript{194} IrCl_{3} without any organic ligands also converted to NPs, which act as true catalysts during the controlled-potential-electrolysis of a phosphate buffer solution (pH 8.0) containing 500 μM Co_{4}POM (red cycle) or 58 μM Co(NO_{3})_{2} (black square) at an applied potential of 1.1 V vs. Ag/AgCl. Reprinted with permission from ref. 214. Copyright 2011, the American Chemical Society.

When 15 was used as a WOC, the yield of O_{2} produced was determined to be 45% based on the initial concentration of Na_{2}S_{2}O_{8} (2[O_{2}]/[Na_{2}S_{2}O_{8}]; [O_{2}]/f is the final O_{2} concentration) containing 500 μM Co_{4}POM (red cycle) or 58 μM Co(NO_{3})_{2} (black square) at an applied potential of 1.1 V vs. Ag/AgCl (pH 8.0).\textsuperscript{214} Such agreement suggests that the Co_{2} ions leached from the Co_{4}POM solution are converted to CoO NPs that act as a true WOC for the electrocatalytic WOR.\textsuperscript{214} Water-soluble cobalt-polyoxometalate (Co-POM) complexes were changed to act as either a homogeneous catalyst or a heterogeneous catalyst for electrocatalytic and photocatalytic WORS.\textsuperscript{215–217} In contrast to water soluble Co-POMs, a water insoluble salt of Co_{9}(H_{2}O)_{6}(OH)_{3}(HPO_{4})(PW_{9}O_{34})_{3} \textsuperscript{16–} (Co_{4}POM) was reported to act as a heterogeneous WOC exhibiting remarkable long-term stability in the solid state.\textsuperscript{218} The barium salt of Co_{9}POM outperforms the state-of-the-art IrO_{2} catalyst even at pH < 1, with an overpotential of 189 mV at 1 mA cm\textsuperscript{–2}.\textsuperscript{219} The catalytic stability in acidic medium was enhanced by using a carbon-paste conducting support with a hydrocarbon binder, which provides a hydrophobic environment.\textsuperscript{219}

Water-soluble cobalt complexes with organic ligands, [Co^{II}(Me_{6}tren)(OH)_{3}]^{2+} (16), [Co^{III}Cp*(bpy)(OH)_{2}]^{2+} (17),
[CoII(12-TMC)]^{2+} (18) or [CoII(13-TMC)]^{2+} (19) (Me₆tren = tris [N,N'-dimethylaminoethyl]amine, 12-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane and 13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane) (Fig. 12), were converted to NPs that act as a true catalyst for the photocatalytic WOR by Na₂S₂O₈ with [Ru(bpy)₃]^{2+}. The O₂ yields in the photocatalytic WOR with 16, 17, 18 and 19 at pH 8.0 were also determined to be 34, 29, 16 and 41%, respectively. The quantum yields of O₂ evolution with 16 and 17 at pH 8.0 were determined to be 32 and 30%, respectively. The oxygen atoms of the evolved O₂ were confirmed to originate exclusively from H₂O by isotope-labelling experiments using H₂¹⁸O.

Photoillumination of an aqueous solution of 16 (50 μM), [Ru(bpy)₃]^{2+} (0.50 mM) and Na₂S₂O₈ (10 mM) with visible light (λ > 420 nm) at pH 9.0 for 3 min resulted in the formation of NPs with the size of ca. 20 nm as detected by DLS measurements (Fig. 13a). The size of NPs produced from 17 was larger in the range of 100–500 nm, which became larger at a longer photoillumination time (Fig. 13b). The size of NPs produced from Co(NO₃)₂ (50 μM) also increased to ca. 500 nm by elongation of the photoillumination time to 30 min as shown in Fig. 13c. These results indicate that NPs are produced from 16, 17 and Co(NO₃)₂ at the early stage of the photocatalytic WOR by Na₂S₂O₈ with [Ru(bpy)₃]^{2+}. TEM images of the NPs formed from 16, 17 and Co(NO₃)₂ agree with the particle size estimated by DLS measurements.

X-ray photoelectron spectra (XPS) of the NPs formed in the photocatalytic WOR by Na₂S₂O₈ with 16 are shown in Fig. 14, where the NPs formed from 16 revealed two intense peaks at 780.0 eV for Co 2p½ and 795.3 eV for Co 2p½ with weak satellite peaks, whereas Co₂O₄ exhibits two strong peaks at 779.8 eV for Co 2p½ and at 795.1 eV for Co 2p½ with small satellite peaks as well. The satellite peaks observed for the NPs are attributed to the higher ratio of Co(II) species compared with the authentic Co₂O₄ sample. The oxygen 1s peak of the NPs was observed at 531.5 eV, which is by 1.2 eV higher than the oxygen 1s peak of Co₂O₄ (530.3 eV). The higher energy of the oxygen 1s peak of the NPs was reported to result from metal hydroxide species. Thus, the surface of the NPs converted from 16 under the photocatalytic WOR by Na₂S₂O₈ consists of Co(OH)₂ that acts as the true WOC for the photocatalytic WOR. TG/DTA measurements indicated the existence of carbonaceous residues in the NPs produced via the oxidation of Me₆tren ligand of 16. Cobalt NPs produced in situ from Co²⁺ ions and methylene diphosphonate in the photocatalytic WOR also exhibited a high catalytic reactivity.
Although 17 was converted to Co(OH)$_2$ NPs in the photocatalytic WOR by Na$_2$S$_2$O$_8$ under alkaline conditions (vide supra),$^{220,221}$ 17 was reported to act as a homogeneous WOC under acidic conditions with Sc(NO$_3$)$_3$ (100 mM), combined with photocatalytic two-electron reduction of O$_2$ for overall WRC to produce H$_2$O$_2$. $^{222}$

In contrast to the case of 16–19, a dinuclear bis-$\mu$-hydroxo Co$^{III}$-(TPA) complex $^{20}$ ([TPA]Co[$\mu$-OH]$_2$Co(TPA))[ClO$_4$]$_3$ ([TPA = tris(2-pyridylmethyl)amine] in Fig. 15) was reported to act as a homogeneous WOC in the photocatalytic WOR by Na$_2$S$_2$O$_8$ with [Ru(bpy)$_3$]$^{2+}$ in borate buffer (pH 8.0). $^{225,226}$ At pH 9, 20 is deprotonated to produce the $\mu$-oxo-$\mu$-hydroxo dinuclear Co$^{III}$ complex, $^{[\text{Co}_{III}(\mu-O)(\mu-OH)](TPA)$_2$}$ $^{20}$-H$^+$. $^{226}$ The two-electron oxidation of $^{[\text{Co}_{III}(\mu-O)(\mu-OH)](TPA)$_2}$ $^{20}$-H$^+$ by two equivalents of [Ru(bpy)$_3$]$^{2+}$ affords the triplet bis-$\mu$-oxyl complex after removal of proton, which is proposed to undergo a spin flip to give a singlet bis-$\mu$-oxyl complex, followed by intramolecular radical coupling between the two oxyl ligands to produce a $\mu$$\eta^2$$\eta^2$-peroxo dinuclear Co$^{III}$ intermediate (Scheme 4). $^{226}$ The reaction of the $\mu$$\eta^2$$\eta^2$-peroxo dinuclear Co$^{III}$ complex with water yields a $\mu$-peroxo-$\mu$-hydroxo dinuclear Co$^{III}$ complex, which is further oxidised by two equivalents of [Ru(bpy)$_3$]$^{2+}$ to evolve O$_2$, accompanied by regeneration of $20$-H$^+$. $^{226}$ The r.d.s. is suggested to be initial proton-coupled electron transfer from $20$-H$^+$ to [Ru(bpy)$_3$]$^{2+}$, precluding the detection of the reactive intermediates in the catalytic cycle in Scheme 4. $^{226}$

On the other hand, EDTA and 2,2′-bipyridine titrations together with scanning electron microscopy (SEM), EDX, ICP-AES, TEM and XPS measurements revealed that 20 is a precursor for Co$_2$ NPs that act as a true WOC. $^{227}$ After the photocatalytic WOR with 20, the solution was taken on the Cu grid to observe traces of CoO$_x$ by TEM. $^{227}$ When a magnetic stirring bar was used during the photocatalytic WOR, no heterogeneous CoO$_x$ could be observed by TEM, because the produced CoO$_x$ adhered on the surface of the magnetic stirring bar. $^{227}$ The presence of CoO$_x$ formed in the photocatalytic WOR would be difficult to detect by DLS measurements. $^{227}$

![Fig. 15 X-ray crystal structure of a bis-$\mu$-hydroxo Co$^{III}$-(TPA) complex (20). Reprinted with permission from ref. 226. Copyright 2016, the American Chemical Society.](Image)

![Fig. 16 Cobalt(III) complexes with tetraamido macrocyclic ligands (21: Na[(TAML)Co$^{III}$] and 22: Et$_4$N[(bTAML)Co$^{III}$]) used for the electrocatalytic WOR in phosphate buffer. Reprinted with permission from ref. 228. Copyright 2018, the American Chemical Society.](Image)

In contrast to the case of 16–19, a dinuclear bis-$\mu$-hydroxo Co$^{III}$-(TPA) complex [20: ([TPA]Co[$\mu$-OH]$_2$Co(TPA))[ClO$_4$]$_3$ (TPA = tris(2-pyridylmethyl)amine] in Fig. 15] was reported to act as a homogeneous WOC in the photocatalytic WOR by Na$_2$S$_2$O$_8$ with [Ru(bpy)$_3$]$^{2+}$ in borate buffer (pH 8.0). At pH 9, 20 is deprotonated to produce the $\mu$-oxo-$\mu$-hydroxo dinuclear Co$^{III}$ complex, [Co$_{III}(\mu-O)(\mu-OH)](TPA)$_2$] $^{20}$-H$^+$. The two-electron oxidation of [Co$_{III}(\mu-O)(\mu-OH)](TPA)$_2$] $^{20}$-H$^+$ by two equivalents of [Ru(bpy)$_3$]$^{2+}$ affords the triplet bis-$\mu$-oxyl complex after removal of proton, which is proposed to undergo a spin flip to give a singlet bis-$\mu$-oxyl complex, followed by intramolecular radical coupling between the two oxyl ligands to produce a $\mu$$\eta^2$$\eta^2$-peroxo dinuclear Co$^{III}$ intermediate (Scheme 4). The reaction of the $\mu$$\eta^2$$\eta^2$-peroxo dinuclear Co$^{III}$ complex with water yields a $\mu$-peroxo-$\mu$-hydroxo dinuclear Co$^{III}$ complex, which is further oxidised by two equivalents of [Ru(bpy)$_3$]$^{2+}$ to evolve O$_2$, accompanied by regeneration of $20$-H$^+$. The r.d.s. is suggested to be initial proton-coupled electron transfer from $20$-H$^+$ to [Ru(bpy)$_3$]$^{2+}$, precluding the detection of the reactive intermediates in the catalytic cycle in Scheme 4. At a high concentration (1 mM), however, the dinuclear Co catalyst remained intact after the photocatalytic WOR as revealed by $^1$H NMR measurements. Thus, whether WOCs are homogeneous or heterogeneous may depend on the concentrations of the catalysts.

Mononuclear cobalt(III) complexes with tetraamido macrocyclic ligands (Na[(TAML)Co$^{III}$] (21): TAML = 3,3,6,9,9-hexamethyl-2,5,7,10-tetraoxo-3,6,7,9,10-hexahydro-2H-benzo[1,4,7,10]-tetraazacyclotridecine-1,4,8,11-tetraide and (Et$_4$N[(bTAML)Co$^{III}$]) (22): bTAML = biuret-modified tetra-amidomacrocyclic ligand) in Fig. 16) were found to act as stable and efficient homogeneous catalysts for the electrocatalytic WOR in phosphate buffer. In 0.10 M phosphate buffer at pH 9.2, CV responses of 22 (0.25 mM) exhibited two irreversible oxidation waves: one at $E_{pa}$ vs. NHE = 1.1 V and the second at $E_{pa}$ vs. NHE = 1.5 V with an enhanced current above the background, indicating a catalytic process. In 0.1 M deuterated phosphate buffer at pH 9.2, the first irreversible wave was shifted by 0.2 V to afford the deuterium kinetic isotope effect (KIE = 8.63), while the second wave remained constant.
Such a large KIE indicates that the first irreversible wave is associated with a concerted proton–electron transfer (CPET) process to produce the Co IV(O) species [eqn (4)]. On the other hand, the second wave is a pH independent ET process to produce the Co V(O) species [eqn (5)].

\[
[b\text{TAML}]\text{Co}^{III}\text{O}^- + \text{H}_2\text{O} - e^- \rightarrow [b\text{TAML}]\text{Co}^{IV}\text{(O)}] + 2\text{H}^+ \quad (4)
\]

\[
[b\text{TAML}]\text{Co}^{IV}\text{(O)}] - e^- \rightarrow [b\text{TAML}]\text{Co}^{V}\text{(O)}]^- . \quad (5)
\]

Due to the redox non-innocent nature of the TAML ligand, the Co IV(O) and Co V(O) species may be better described as \([b\text{TAML}]\text{Co}^{III}\text{O})\) or \([b\text{TAML}]\text{Co}^{III}\text{(O)}\), respectively. The electron-transfer oxidation of 21 by one-electron oxidants such as copper(II) triflate, \([\text{Fe}^{III}\text{(bpy)}])_3^{17}\), tris(4-bromophenyl)ammoniumyl radical cation and CAN \((E_{\text{red}} = 1.4 \text{ V vs. SCE})\) with \(\text{H}_2\text{O}\) resulted in the formation of \([(\text{TAML})\text{Co}^{IV}\text{(O)}]^{2-}\) which was detected by EPR. In any case, the two-electron oxidised species is likely the key intermediate responsible for O–O bond formation in the WOR catalytic cycle, as the case of the Ru V(O) species in Scheme 1.

The \(O_2\) evolution was confirmed by bulk electrolysis at \(+1.40 \text{ V} \) vs. Ag/AgCl on an ITO electrode with a large surface area (1 cm\(^2\)) and using 21 (1 mM) in phosphate buffer (pH 7.0) as shown in Fig. 17 (blue line), where an induction period was observed for \(O_2\) evolution. It was confirmed that \(O_2\) evolution was negligible without 21 (black line). Although the Faraday efficiency of \(O_2\) evolution was higher than 90%, the \(O_2\) yield (250 \(\mu\text{M}\)) at 4000 s was much smaller than the catalyst concentration (1 mM) with a TON of less than 1. The induction period may indicate the formation of heterogeneous CoO\(_x\) that may be much more active than the starting homogeneous catalyst. However, the X-ray photoelectron spectroscopic (XPS) measurements exhibited no signal due to CoO\(_x\) formed on the ITO electrode after bulk electrolysis. SEM of the ITO surface topography also indicated that no CoO\(_x\) was precipitated during the electrolysis.

Whether 21 and 22 act as homogeneous WOCs or precursors of heterogeneous NP catalysts should also be checked for the homogeneous photocatalytic WOR by Na\(_2\)S\(_2\)O\(_5\) with \([\text{Ru(bpy)}])_3^{21}\). Cobalt porphyrins and corroles were also reported to act as efficient homogeneous catalysts for the WOR under basic conditions. However, the combination of electrochemistry, UV-vis, SEM, energy-dispersive X-ray spectroscopy (EDS), and synchrotron-based photoelectron spectroscopy (SOXPES and HAXPES) indicated that cobalt porphyrins, which were deposited on FTO glasses, were readily decomposed into a thin film of CoO\(_x\) on the surface of the electrode during the electrocatalytic WOR in a borate buffer solution (pH 9.2). The UV-vis, SEM, and EDS measurements are not sensitive enough for the detection of CoO\(_x\) on the FTO electrode. In order to detect CoO\(_x\) on the FTO electrode, adjusting the photon energy of the XPS to 1000 eV (SOXPES) was crucial in order to provide a high surface sensitivity. A high TOF of 10 s\(^{-1}\) was obtained for the electrocatalytic oxidation of water using the CoO\(_x\)/FTO electrode derived from cobalt porphyrins.

### 3.3. Manganese complexes

Manganese complexes have been extensively studied as functional mimics of the OEC in PSII in the past few decades. For example, a dinuclear manganese complex, \([\text{Mn}(\text{OAc})_2(\text{bpmp})]^{+}\) \((\text{bpmp} = 2,6-\text{bis}[\text{N,N-di(2-pyridylmethyl)}\text{amino}]-\text{methyl}-1,4-\text{methylphenol anion})\), was reported to act as a homogeneous catalyst for the WOR by oxone (HSO\(_5\)) to evolve \(O_2\) together with CO\(_2\) due to ligand oxidation. In this reaction, manganese complexes (23 and 24 shown in Fig. 18) were converted to manganese oxide (MnO\(_x\)) NPs as a true catalyst during the catalytic WOR by CAN. The MnO\(_x\) NPs were characterised by XPS, EPR, FTIR, TEM, SEM and XRD measurements.

Highly dispersed MnO\(_x\) NPs with the size of 10–20 nm and 6–10 nm were also produced from \([\text{Mn}((\text{Me}_3\text{TACN})(\text{OMe}))_3]^{+}\) and \([\text{Me}_2\text{TACN}][\text{Mn}_{\text{II}}^{\text{II}}(\mu-\text{O})(\mu-\text{CH}_3\text{COO})_2]^{2+}\) \((\text{Me}_2\text{TACN} = \text{N}_2\text{N}_2\text{N}^-\text{trimethyl-1,4,7-triazacyclononane})\), respectively, via the dissociation of the complexes into Mn(u) species that were oxidised by applying an external bias potential. The electrochemical oxidation of \([\text{Mn}((\text{OH}))_2]^{2+}\) also resulted in the generation of MnO\(_x\) NPs with the size of 30–100 nm, which were less active WOCs. A TOF of more than 100 molecules of \(O_2\) Mn\(^{-1}\) s\(^{-1}\) was achieved for MnO\(_x\) NPs with the smaller size of ca. 10 nm.

![Fig. 17](image1.png) Time profile of \(O_2\) evolution in the course of bulk electrolysis of a 0.10 M phosphate buffer solution (pH 7.0) of 1.0 mM \([\text{TAML}][\text{Co}])\) (21) at an applied potential of 1.40 V vs. Ag/AgCl on the ITO electrode (1.0 cm\(^2\)). Reprinted with permission from ref. 228. Copyright 2018, the American Chemical Society.

![Fig. 18](image2.png) Manganese complexes used as precursors for the catalytic WOR by CAN.
A water-soluble manganese–potassium (Mn–K) cluster, [Mn$_8$K$_2$(μ-O)$_4$μ-OH)$_2$]($\text{Piv}$)$_{16}$($\text{Piv}$-$\text{H}$)[(CH$_3$CN)], [Piv-$\text{H}$ = pivalic acid], was also converted to MnO$_x$ NPs, which were characterised by using X-ray absorption spectroscopy (XPS), SEM, TEM, FTIR, X-ray diffraction and electrochemical methods.\textsuperscript{250} MnO$_x$ NPs thus produced act as true catalysts for the electrocatalytic WOR.\textsuperscript{250}

Molecular catalysis for the WOR was recently reported for manganese porphyrin dimers with mono- and hexaphosphonic acid groups (Mn$_2$DP-PO$_3$H$_2$ and Mn$_2$DP(PO$_3$H)$_3$)$_2$), which were covalently assembled on the surface of the ITO electrode (ITO = indium-doped tin oxide). The Mn$_2$DP-PO$_3$H$_2$/ITO assemblies showed high TOF (up to 47.4 s$^{-1}$) at a low overpotential ($\eta$ = 0.26 V) at pH 1.5.\textsuperscript{251} The robustness of the catalyst was much improved when Mn$_2$DP(PO$_3$H)$_3$/ITO assemblies were used as the WOC for the sake of the increased number of phosphonic acid anchor groups.\textsuperscript{251} The Mn$^V$(O) species were proposed to be the reactive intermediate for the WOR to form the O–O bond by the nucleophilic attack of water as the case of the Ru$^V$(O) species in Scheme 1.\textsuperscript{251} It was demonstrated that the addition reaction of the hydroxide ion to the Mn$^V$(O) species derived from the manganese(III) corrole complexes, [TPFC]Mn$^{III}$] (TPFC = 5,10,15-tris(pentafluorophenyl)corrolato trianion), afforded the Mn$^IV$-peroxo species via O–O bond formation and the resulting Mn$^IV$-peroxo species reverted to the Mn$^V$(O) species upon the addition of proton, indicating that the O–O bond formation and cleavage reactions between the Mn$^V$(O) and Mn$^IV$-peroxo complexes were reversible.\textsuperscript{252–254} On the basis of hybrid density functional calculations, however, the crucial O–O bond formation proceeds from the formal Mn$^IV$-$\mu$-$\text{O}$-$\mu$-$\text{peroxo}$ state of a tetraneutral Mn complex by direct coupling of a Mn$^IV$-bound terminal oxyl radical and a di-Mn bridging oxo group,\textsuperscript{255} which is a mechanism quite similar to that proposed for the natural system.\textsuperscript{256}

### 3.4. Iron complexes

Extensive efforts have been made to develop efficient WOCs composed of more Earth-abundant metals than Co, such as Mn,\textsuperscript{240–254} Ni,\textsuperscript{257–261} Cu,\textsuperscript{262–271} and Fe\textsuperscript{272–276} (vide infra). Among Earth-abundant metals, Fe is the most Earth-abundant and environmentally friendly metal, and is commonly employed as a catalyst for organic substrate oxidation by metalloenzymes and metal catalysts.\textsuperscript{277–281} Mononuclear Fe complexes with tetradentate N donor ligands containing H$_2$O coordination sites (25 and 26 in Fig. 19) exhibited high catalytic activity for the WOR by CAN with maximum TON values of 360 and 145 with 25 and 26, respectively, at pH 1.0.\textsuperscript{284} The TON value is limited by the demetallation associated with the ligand dissociation of the iron complexes under acidic conditions, and the dissociated ligands were oxidised by CAN to yield CO$_2$.\textsuperscript{284,285} In competition with the ligand oxidation, the iron(IV)-oxy species was produced as the reactive intermediate for the O–O bond formation in the catalytic WOR, being detected by UV-vis absorption and electrospray ionization mass spectrometer (ESI-MS) measurements.\textsuperscript{284} DLS measurements and NP-tracking analysis (NTA) indicated no appreciable formation of iron oxide NPs when 25 acted as a homogeneous WOC during the WOR.\textsuperscript{284}

Other iron complexes, such as [Fe(bpy)$_2$Cl$_2$]Cl, [Fe(tpy)$_2$Cl$_2$] (tpy = 2,2′,6,2′-terpyridine), cis-[Fe(cyclen)Cl$_2$] (cyclen = 1,4,7,10-tetraazacyclododecane) and trans-Fe(TMC)Br$_2$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), can also catalyse the WOR by a one-electron oxidant such as [Ru(bpy)$_3$]$^{3+}$ to evolve O$_2$ at pH 7–9.\textsuperscript{286} These Fe(III) complexes can also be used as a WOC for the photocatalytic WOR by Na$_2$S$_2$O$_8$ with [Ru(bpy)$_3$]$^{3+}$ (Scheme 3).\textsuperscript{285,286} However, Fe(ClO$_4$)$_2$ without organic ligands acted as a precursor of a true WOC and afforded the largest O$_2$ yield (48%), when NPs (500–1200 nm) composed of FeO$_x$, which was identified by energy-dispersive X-ray spectroscopy and XPS measurements, were observed in DLS measurements.\textsuperscript{286} Thus, the true catalysts derived from the Fe(III) complexes with tetradentate N donor ligands in the thermal and photochemical WORS are different depending on the pH of reaction solutions.\textsuperscript{285,286} The iron(IV)-oxy species produced as the reactive intermediate for the O–O bond formation in the catalytic WOR is unstable at high pH, where Fe complexes undergo hydrolysis, accompanied by the ligand oxidation to generate Fe$_3$O$_4$, which is the true catalyst for the catalytic WOR at high pH.\textsuperscript{286}

A Fe$^{III}$ complex of the biuret-modified tetra-amidomacrocyclic ligand ([bTAML]Fe$^{III}$)$^{2+}$ was also used as a WOC in the photochemical WOR by Na$_2$S$_2$O$_8$ with [Ru(bpy)$_3$]$^{3+}$ (Scheme 3) in pH 8.7 borate buffer to afford TON = 220 ± 10 and ∼44% O$_2$ yield.\textsuperscript{287} The higher TON of 900 and the O$_2$ yield of 48% with the quantum yield of 24% were obtained by using an inorganic molecular tetra-iron(m)-substituted polyoxotungstate Fe$_{12}$(H$_2$O)$_{10}$[(P$_2$W$_{12}$O$_{46}$)$_{12}$]$_{12}^{32-}$ in pH 9.0 borate buffer.\textsuperscript{286} In both cases, no evidence of iron oxide NPs was observed by DLS or TEM measurements.\textsuperscript{287,288} The molecular catalytic mechanism of ([bTAML]Fe$^{III}$)$^{2+}$ is proposed as shown in Scheme 5,\textsuperscript{287} where photoexcitation of [Ru(bpy)$_3$]$^{3+}$ results in ET from S$_2$O$_8^{2-}$ to the excited state ([Ru(bpy)$_3$]$^{3+}$)* to produce [Ru(bpy)$_3$]$^{3+}$ and SO$_4^{2-}$.\textsuperscript{289} Then, ET from [bTAML]Fe$^{III}$ to [Ru(bpy)$_3$]$^{3+}$ occurs with H$_2$O to produce [bTAML]Fe$^{V}$[OH]$_2$ after the deprotonation, accompanied by the regeneration of [Ru(bpy)$_3$]$^{3+}$.\textsuperscript{287} Two ([bTAML]Fe$^{V}$[OH]$_2$) molecules are converted to the μ-oxo dimer ([bTAML]Fe$^{IV}$[O]Fe$^{IV}$[bTAML]$^{3+}$) after removal of H$_2$O. Although the μ-oxo dimer is not further oxidised by...
[Ru(bpy)]^{3+\text{+}} \text{, it is oxidised by SO}_{4}^{2-} \text{ to produce the Fe}^{V}(O) \text{ species ([][[bTAML]FeV(O)]^{2-}})\text{.}^{287}\text{ When [[bTAML]FeV(O)]^{2-} \text{ is present, a fast comproportionation reaction of [[bTAML]FeV(O)]^{2-} \text{ with }}[[bTAML]Fe^{III}]^{2-} \text{ occurs to produce the μ-oxo dimer ([][[bTAML]Fe^{IV}(O)Fe^{IV}(bTAML)]^{2-})\text{.}^{290}\text{ Then, the nucleophilic attack of water on the Fe}^{V}(O) \text{ species occurs to produce the mononeric Fe}^{III}-\text{hydroperoxo species ([[bTAML]Fe^{III}(OOH)]^{2-})\text{ as the case of the Ru}^{II}(O) \text{ species in Scheme 1}\text{.}^{287}\text{ Although the Fe}^{V}(O) \text{ species ([[bTAML]FeV(O)]^{2-}) \text{ was not detected in water due to the instability, the formation of [[bTAML]FeV(O)]^{2-} \text{ was detected by HRMS and EPR when the photochemical WOR was performed using equimolar amounts of [[bTAML]Fe^{III}], [[Ru(bpy)]^{3+\text{+}} \text{ and Na}_{2}S_{2}O_{8} (60 \text{ μM each}) in CH}_{3}CN-buffer (v/v 1:1)\text{.}^{287}\text{ HRMS revealed two peaks: one for the unreacted Fe}^{III} \text{ complex (m/z = 431.08 for [[bTAML]Fe^{III}]^{2-}) and the other for the Fe}^{V}(O) \text{ complex (m/z = 429.07 for }}[[bTAML]Fe^{IV}(O)Fe^{IV}(bTAML)]^{2-}) \text{ within the instrumental error limit, which was shifted to 431.08 when H}_{2}O \text{ was used instead of H}_{2}^{18}O.\text{287}\text{ Both [[TAML]Fe}^{III}]^{2-} \text{ and [[bTAML]Fe}^{III}]^{2-} \text{ can also catalyse the WOR by cerium(IV) ammonium nitrite (CAN) at pH 1 to evolve oxygen with 14% and 4% yields, respectively.}^{287,291}\text{ The low oxygen yields result from the facile demetallation with a strong acid at pH 1.}^{287,291}\text{ The initial oxygen evolution rates were proportional to the concentrations of [[TAML]Fe}^{III}]^{2-} \text{ and [[bTAML]Fe}^{III}]^{2-},^{287,291} \text{ indicating that r.d.s. is a nucleophilic attack of water on the Fe}^{III} \text{ species rather than a radical coupling process.}^{291}\text{ [[bTAML]Fe}^{III}]^{2-} \text{ also acts as an efficient catalyst for the electrochemical WOR to evolve O}_{2} \text{ with an overpotential of about 250 mV at pH 7.}^{292}\text{ [[bTAML]Fe}^{III}]^{2-} \text{ exists as a six-coordinate complex ([[bTAML]Fe^{III}(H}_{2}O)_{2}]) \text{ with both the water molecules located at the axial positions of Fe}^{III}.^{292,291}\text{ The pK}_{a} \text{ value of the axial H}_{2}O \text{ ligands of ([[bTAML]Fe^{III}(H}_{2}O)_{2}]) \text{ in water was determined to be 10.3 by UV-vis titration experiments.}^{292}\text{ The cyclic voltammogram of ([[bTAML]Fe^{IV}(H}_{2}O)_{2}]) \text{ exhibited the first oxidation peak potential at 0.85 V vs. NHE at pH 7 and the peak potential decreased with increasing pH by about 117 mV (pH unit) between pH 7 and 10.}^{292}\text{ This indicates a proton-coupled electron-transfer (PCET) oxidation of ([[bTAML]Fe^{III}(H}_{2}O)_{2}]) \text{ is associated with removal of two protons to produce ([][[bTAML]Fe}^{IV}(O)(H}_{2}O)]^{2-} \text{ [eqn (6)] as in the case of (\text{6})\text{.}^{292}\text{ ([][[bTAML]Fe}^{IV}(O)(H}_{2}O)]^{2-} \text{ − e}^{-} \rightarrow ([][[bTAML]Fe}^{V}(O)(H}_{2}O)]^{2-} + 2H^{+}\text{ (6)\text{.}^{292}\text{ When H}_{2}O \text{ was replaced by D}_{2}O, the first irreversible wave was shifted by 80 mV to afford the deuterium kinetic isotope effect (KIE = 3.2).}^{292}\text{ The KIE indicates that the O−H/O−D bond cleavage is involved in the PCET process in eqn (6). The second oxidation peak was observed at 1.25 V vs. NHE at pH 7 with a drastically enhanced current above the background. This oxidation peak potential was pH-independent between pH 7 and 10, corresponding to the one-electron oxidation of ([][[bTAML]Fe}^{IV}(O)(H}_{2}O)]^{2-} \text{ to the Fe}^{V}(O) \text{ species ([[bTAML]Fe}^{V}(O)(H}_{2}O)]^{2-} \text{ [eqn (7)]. Controlled-potential electrolysis of 1 mM ([][[bTAML]Fe}^{III}(H}_{2}O)_{2}]) \text{ in pH 7.2 phosphate buffer (15 mm) on 1 cm}^{-2} \text{ platinum foil at 1.26 V vs. NHE for 2 h afforded a total charge of 0.8 C to yield 186 μM of O}_{2}, \text{ which corresponds to 89.9% faradaic efficiency.}^{292}\text{ Although the formation of the Fe}^{V}(O) \text{ species was not detected during the electrolysis in pure water, electrolysis of ([][[bTAML]Fe}^{III}(H}_{2}O)_{2}]) \text{ in CH}_{3}CN/H}_{2}O (v/v 9:1) \text{ at 1.25 V vs. NHE for 60 s resulted in the formation of the Fe}^{V}(O) \text{ species ([[bTAML]Fe}^{V}(O)(H}_{2}O)]^{2-} \text{), which was detected using the characteristic UV-vis peaks at 445 and 613 nm as well as by HRMS.}^{292}\text{ ([][[bTAML]Fe}^{V}(O)(H}_{2}O)]^{2-} \text{ − e}^{-} \rightarrow ([][[bTAML]Fe}^{V}(O)]^{2-} + H_{2}O\text{ (7)\text{.}^{292}\text{ The highest TOF value (1900 s}^{-1} \text{) was reported using a pentanuclear iron complex, [Fe}_{4}^{II}Fe^{III}[μ-O][μ-L]_{6}^{3+} (LH = 3,5-bis(2-pyridyl)pyrazole), in an acetonitrile/water (10:1) mixed solution with Et}_{4}NClO_{4} (0.10 M).}^{294}\text{ However, the large overpotential (η = 0.5 V) has precluded practical application.}^{294}\text{ The overpotential was reduced to 340 mV at 10 mA cm}^{-2} \text{ in 1.0 KOH aqueous solution using Fe(TCNQ)]_{2} \text{ (TCNQ = tetracyanoquinodimethane), which is a conductive MOF showing long-term electrochemical durability with its catalytic activity retained for at least 110 h.}}^{295}\text{4. Mixed metal oxide nanoparticles}\text{As mentioned above, manganese-oxo-calcium clusters (Mn}_{6}CaO_{5} \text{ catalyse efficiently the WOR by the OEC in PSII.}^{84-93}\text{ The Ca}^{2+} \text{ ion in the OEC is proposed to play a pivotal role to regulate the oxidising reactivity of the Mn}^{IV}(O) \text{ reactive intermediate based on studies of metal ion-coupled electron-transfer (MCET) reactions.}^{296-302}\text{ Inspired by the important role of Ca}^{2+} \text{ ions, redox-inactive metal ions were introduced to metal oxides to generate mixed metal oxides to enhance the WOR catalytic activity. This naive idea was tested by using per-}
ovskite (LaCoO₃, NdCoO₃, YCoO₃, and La₀.₅Sr₀.₅CoO₃) and wolframite (CoWO₄) as WOCs in comparison with spinel (Co₃O₄) for the photochemical WOR by Na₂S₂O₈ with [Ru(bpy)₃]²⁺, as shown in Fig. 20.³⁰³

The decay rates of [Ru(bpy)₃]³⁺ in the WOR with LaCoO₃ (brown) and La₀.₅Sr₀.₅CoO₃ (red) are faster than that without catalyst.³⁰³ The O₂ yields in the photocatalytic WOR by Na₂S₂O₈ with [Ru(bpy)₃]²⁺ using LaCoO₃, CoWO₄, Co₃O₄ and La₀.₅Sr₀.₅CoO₃ as WOCs at pH 7.0 were 74%, 19%, 59% and 47%, respectively (Fig. 20b).³⁰³ Among cobalt-containing mixed metal oxides, LaCoO₃ exhibited the highest WOR catalytic activity.³⁰³

Partial replacement of La³⁺ with Sr²⁺ resulted in the formation of CoIV species in a cobalt-containing perovskite, leading to a decrease in the catalytic activity.³⁰³ On the other hand, replacement of La³⁺ with Nd³⁺ and Y³⁺ resulted in no significant change in the catalytic activity of NdCoO₃ and YCoO₃ as compared with LaCoO₃.³⁰³ Thus, the trivalent metal ions acting as strong Lewis acids enhanced the oxidation activity of CoIV species for the WOR.³⁰³

The catalytic reactivity for photocatalytic WOR by Na₂S₂O₈ with [Ru(bpy)₃]²⁺ was also improved by doping Ni²⁺ ions to iron oxides used as a WOC. Although the catalytic activity of Fe₂O₃ is lower than those of Fe₃O₄ and Co₃O₄ in the photocatalytic WOR as shown in Fig. 21a, NiFe₂O₄ NPs exhibited the highest catalytic activity with the largest O₂ yield (74%) as compared with MgFe₂O₄ and MnFe₂O₄ NPs (Fig. 21b).³⁰⁴ Recycling of NiFe₂O₄ NPs showed no significant change in the total amount of O₂ evolution in the 2nd and 3rd runs from the reaction solutions, demonstrating that NiFe₂O₄ acts as an efficient and robust catalyst for the photocatalytic WOR.³⁰⁴

The NiFe₂O₄ NPs/NiFe layered double hydroxide (LDH) nanosheet heterostructure array on Ni foam was reported to display high catalytic activity toward the OER with a very small overpotential of 213 mV at 100 mA cm⁻².³⁰⁵ It also exhibits outstanding HER activity with a very small overpotential of 101 mV at 10 mA cm⁻².³⁰⁵ The NiFe₂O₄ NPs/NiFe LDH nanosheet array electrodes also exhibit excellent stability against OER, HER and also the overall water splitting at large current densities. The overall water splitting with NiFe₂O₄ NPs/NiFe LDH nanosheets employed as both the anode and the cathode can be continuously driven by a battery of 1.5 V.³⁰⁵

The most efficient catalyst for the photocatalytic WOR in a buffer solution (pH 7.0) containing [Ru(bpy)₃]²⁺ and Na₂S₂O₈ was obtained by the incorporation of a small amount of Ca²⁺ ions into a polymeric cobalt cyanide complex to form Ca₃[CoII(H₂O)₆]₁.₄₄[CoIII(CN)₆] (27 in Fig. 22).³¹⁶ The maximum quantum efficiency of 200% was achieved by using Ca₃[CoII(H₂O)₆]₁.₄₄[CoIII(CN)₆] as a WOC when one photon absorption of [Ru(bpy)₃]²⁺ with Na₂S₂O₈ results in the generation of two molecules of [Ru(bpy)₃]³⁺ (Scheme 3).³¹⁶

The lowest overpotential of 65 mV at 10 mA cm⁻² for the WOR was achieved by using binary Ni–Fe sulphones supported on nickel foam (NF) used as a WOC in 0.10 M KOH.³¹⁷ However, the NiFe/NF catalyst was not stable due to the

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**Fig. 20** (a) Decay time profiles of absorbance at 670 nm due to [Ru(bpy)₃]³⁺ (0.20 mM) in the absence and presence of a cobalt–containing mixed metal oxide, WOC (63 mg L⁻¹; black, none; red, La₀.₅Sr₀.₅CoO₃; brown, LaCoO₃), in a phosphate buffer solution (pH 7.0) at 298 K. (b) O₂ evolution time profile of the photocatalytic WOR by Na₂S₂O₈ (5.0 mM) with [Ru(bpy)₃]²⁺ (0.25 mM) and a cobalt–containing mixed metal oxide, WOC (0.25 g L⁻¹; CoO₂ (black), LaCoO₃ (brown), La₀.₅Sr₀.₅CoO₃ (red) and CoWO₄ (blue)) under visible light irradiation (λ > 420 nm) of a phosphate buffer solution (pH 7.0) with a Xe lamp. Reprinted with permission from ref. 303. Copyright 2012, the Royal Society of Chemistry.

**Fig. 21** (a) O₂ evolution time profiles of the photocatalytic WOR by Na₂S₂O₈ (5.0 mM) with [Ru(bpy)₃]²⁺ (0.25 mM) and Fe₂O₃, Fe₃O₄ or Co₃O₄ as a WOC (0.50 g L⁻¹) under photoradiation of a phosphate buffer solution (pH 8.0) with a xenon lamp (λ > 420 nm) at room temperature in three recycling examinations. (b) O₂ evolution time profiles with a WOC (NiFe₂O₄, MgFe₂O₄ or MnFe₂O₄) under the same experimental conditions as those of (a). Reprinted with permission from ref. 304. Copyright 2012, the American Chemical Society.
intrinsic nature of metal sulphides in alkaline solution.\textsuperscript{317} Electrodeposition of Fe hydroxide films on NiFeS/NF(NiFeS–Fe/NF) was performed to protect NiFeS/NF for a better stability during the electrocatalytic WOR. The enhanced stability was compensated for by the lower activity with the higher overpotential of 101.6 mV at 10 mA cm\textsuperscript{–2}.\textsuperscript{317}

5. Conclusions

Whether WOCs are homogeneous or heterogeneous is determined by metals, supporting ligands, pH, oxidants and even concentrations of WOCs. A mononuclear ruthenium polyoxometalate complex (RuPOM) acts as a homogeneous WOC for the WOR by CAN because the inorganic POM ligand is difficult to be oxidised during the catalytic WOR. The kinetic analysis together with the detection of the Ru\textsuperscript{V}(O) intermediates indicates that the r.d.s. of the catalytic WOR is the nucleophilic attack of water on the Ru\textsuperscript{V}(O) intermediate. In contrast, organic ligands of Ir(III) complexes were oxidised during the photocatalytic WOR by Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} with [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}, where iron complexes act as homogeneous WOCs in the catalytic WOR by CAN, although the catalyst lifetime was short due to the deactivation of the photocatalytic WOR by CAN because the inorganic POM ligand is difficult to be oxidised during the catalytic WOR by CAN acting as a much more active WOC than the precursors. In contrast, some Fe(n) complexes act as homogeneous WOCs in the catalytic WOR by CAN, although the catalyst lifetime was short due to the deactivation reaction under acidic conditions. Under alkaline conditions, however, the Fe(n) complexes act as precursors for the photocatalytic WOR by Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} with [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}, where iron oxide NPs were produced to act as a true WOC. The organic ligands of Co(n) complexes were also oxidised in the photocatalytic WOR by Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} with [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} at pH 7–8 to produce Co(OH)\textsubscript{3} NPs acting as an actual WOC. MnO\textsubscript{2} NPs were also produced via the oxidation of organic ligands of Mn complexes during the catalytic WOR by CAN, acting as a much more active WOC than the precursors. In contrast, some Fe(n) complexes act as homogeneous WOCs in the catalytic WOR by CAN, although the catalyst lifetime was short due to the deactivation reaction under acidic conditions. Under alkaline conditions, however, the Fe(n) complexes act as precursors for the photocatalytic WOR by Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} with [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}, where iron oxide NPs were produced to act as a true WOC. Bioinspired by the pivotal role of Ca\textsuperscript{2+} in the OEC in PSI, mixed metal oxide NPs composed of redox-active metal ions and redox-inactive metal ions have been developed as efficient WOCs. The highest catalytic activity for the photocatalytic WOR by Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} was achieved by the incorporation of a small amount of Ca\textsuperscript{2+} ions into a polymeric cobalt cyanide complex to form Ca\textsubscript{2}[Co\textsuperscript{III}(H\textsubscript{2}O)\textsubscript{3}–5][Co\textsuperscript{III}(CN)\textsubscript{6}] [Fig. 22]. The interdisciplinary approach between the homogeneous and heterogeneous WOCs will enhance research progress towards the clarification of the catalytic mechanism and intermediates as well as practical applications of WOCs in order to meet the rapidly growing demand for the development of sustainable solar fuels via WORs.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


J. Barber, Biochemistry, 2016, 55, 5901–5906.


