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Recent advances in ruthenium complex-based light-driven water oxidation catalysts

Long-Xin Xue [a,b], Ting-Ting Meng [a], Wei Yang [a], Ke-Zhi Wang [a,*]

[a] *Beijing Key Laboratory of Energy Conversion and Storage Materials and College of Chemistry, Beijing Normal University, Beijing 100875, China*
[b] *Xichang Satellite Launch Center, Sichuan, China*

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ABSTRACT

The light driven splitting of water is one of the most attractive approaches for direct conversion of solar energy into chemical energy in the future. Ruthenium complexes as the water oxidation catalysts (WOCs) and light sensitizers have attracted increasing attention, and have made a great progress. This mini-review highlights recent progress on ruthenium complex-based photochemical and photoelectrochemical water oxidation catalysts. The recent representative examples of these ruthenium complexes that are in homogeneous solution or immobilized on solid electrodes, are surveyed. In particular, special attention has been paid on the supramolecular dyads with photosensitizer and WOC being covalently hold together, and grafted onto the solid electrode.

1. Introduction

Our modern society is facing formidable challenge of energy crisis and environmental pollution caused by fossil fuels. Solar energy is the most attractive renewable, clean and inexhaustible energy source. Therefore, efficient storage and conversion of solar energy into the chemical energy and electricity by the artificial photosynthesis is an attractive approach to solve these problems. To harness the visible light of the solar spectrum, transition metal complexes that are strongly absorptive in the visible region holds very potential for practical application as sensitizer for inorganic semiconductors one way to convert solar energy into a chemical fuel is the light-driven splitting of water ($H_2O + h\nu = H_2 + O_2$), which has led to very intensive research efforts [1–4]. The water splitting process consists of two half reactions of proton reduction (Eq. (1)) and water oxidation (Eq. (2)):

$$2H^+ + 2e^- \rightarrow H_2 \ (E^\circ = 0.00 \text{ V vs. SHE at pH } 0) \quad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \ (E^\circ = 1.23 \text{ V vs. SHE at pH } 0) \quad (2)$$

As a result, the water splitting overall reaction is a thermodynamically uphill reaction, requiring a minimum energy input corresponding to a potential of 1.23 V at pH 0. In practice, the water oxidation reaction is not only a thermodynamically but also a kinetically demanding process. In order to decompose water into hydrogen catalytically, the water oxidation to oxygen is also necessary by giving protons that can feed for producing hydrogen, and four electrons or gaining four holes (h^+). Importantly, the water oxidation step is thought to be the bottleneck of the whole water splitting process due to its biggest challenging reaction route including a four successive electron transfer and formation of highly reactive oxygen intermediates and an O–O bond [5].

Extensive efforts have been made to develop water oxidation catalysts (WOCs) that minimize the overpotential required to achieve efficient water oxidation. Since pioneering work of Meyer and coworkers in the early 1980s on a $Ru^{III}(\mu\text{-}O)Ru^{III}$ core-containing catalyst of $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{III}(H_2O)(bpy)_2]^{4+}$ (bpy is 2,2′-bipyridine) [6], a large number of ruthenium-based WOCs have been reported with promising chemically, electrochemically and photoelectrochemically-driven water oxidation/splitting catalytic properties [7–11]. However, compared with chemically- and electrochemically-driven water oxidation/splitting, light-driven water oxidation by utilization of solar energy as light source is more desirable in view of above-mentioned advantages of solar energy, and has attracted ever-increasing interest. On the other hand, in order to harness the visible part of the solar spectrum, ruthenium complexes, as the excellent representative of the visible light strongly adsorbed transition metal complexes, can also act as light sensitizers. The ruthenium-based catalytic and sensitized moieties interplay well for the water oxidation, and the records for the water oxidation performance has been set for this family of complexes. In view of some elegant reviews on this respect have appeared [1–4,12–18], this review will give an overview on the representative examples

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* Corresponding author.
E-mail address: kzwang@bnu.edu.cn (K.-Z. Wang).

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of ruthenium complex-based WOCs reported from 2010. Although the attention will be paid on the topic of light-driven water oxidation, chemically or electrochemically driven water oxidation will be occasionally commented, because they are very closely related to light-driven water oxidation properties. As shown in Fig. 1, at least three key components including light absorption unit-photosensitizer (PS), WOC and a sacrificial electron acceptor are required to perform water oxidation functionality. The catalytic systems composed of these three components could work in homogeneous fluid solution or on modified electrodes in the forms of thin films. The Ru complex-based WOCs that are classified into above-mentioned two categories, will be reviewed as follows.

2. Light driven water oxidation in homogeneous fluid solution

2.1. Isolated three-component systems composed of a PS, a WOC and a sacrificial electron acceptor

The light-driven water oxidation is very challenging due to the fact that it requires sequential photo-induced charge separation, transportation and electron transfer from WOCs to PSs [4]. The system includes following three key components: ruthenium-based PS (Ru_P) used mostly is $[Ru(bpy)_3]^{2+}$, sacrificial electron acceptor and ruthenium-based water oxidation catalyst (Ru_C) (see Fig. 1 top). The molecular structures of representative Ru(II) complexes tested for WOCs in three-component system in a homogeneous fluid solution, **1**–**25** are listed in Fig. 2. But only few of them exhibited visible light-driven water oxidation. The WOCs should be chemically stable enough, and competent with other side reactions, and PS should have efficient solar light-harvesting ability. The electrochemical properties and the catalytic activities of these WOCs measured in homogenous medium for light driven water oxidation by using $[Ru(bpy)_3]^{3+}$ as a PS, and persulfate ($S_2O_8^{2-}$) or less frequently $[Co^{III}(NH_3)_5Cl]^{2+}$ as a sacrificial electron acceptor, are compared in Table 1. However, as shown by Eqs. 3–5, $S_2O_8^{2-}$ as an efficient and frequently used sacrificial electron acceptor can form sulfate radicals that have higher potentials (>3.45 V vs. NHE) than the oxidized $[Ru(bpy)_3]^{3+}$ and that may cause side reactions [17]

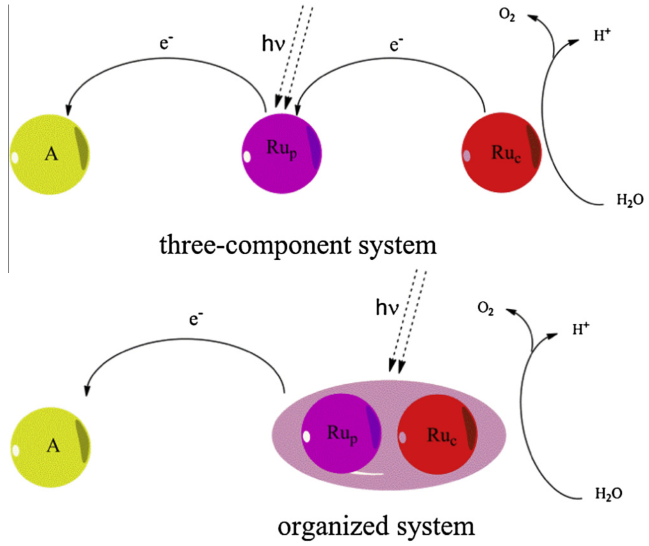

Fig. 1. Cartoons illustrating an isolate three-component system (top panel), in which "A", "Ru_P" and "Ru_C" represents a sacrificial electron acceptor, photosensitizer and water oxidation catalyst, respectively; and an organized system (bottom panel) composed of covalently linked "Ru_P" and "Ru_C".

$$[Ru(bpy)_3]^{2+} + h\nu \rightarrow [Ru(bpy)_3]^{2+*} \tag{3}$$

$$[Ru(bpy)_3]^{2+*} + S_2O_8^{2-} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{-} + SO_4^{2-} \tag{4}$$

$$[Ru(bpy)_3]^{2+} + SO_4^{-} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{2-} \tag{5}$$

Moreover, under the strongly oxidation conditions and light irradiation, many organic ligands of transition metal complex-based WOCs show degradation or photodissociation, resulting in relatively low TONs [18]. As can be seen from Table 1, seven of WOCs listed in Table 1 have TONs less than 15 and only less than half of them achieved TONs larger than 100. In addition, most of the catalysts used PSs with higher oxidation potentials except only six catalysts (**2**, **3**, **12**, **13**, **20**, **21**) can catalyze water oxidation at the potential generated by $[Ru(bpy)_3]^{2+}$, 1.26 V vs. NHE (Table 1). Notably, dinuclear ruthenium complex **20** (Table 1 and Fig. 2) designed and synthesized by Sun and coworkers is indeed a very stable and efficient catalyst for light-driven water oxidation, in fact far superior to other catalysts in Table 1 [27]. Sun and coworkers have reported a series of mononuclear Ru(II) complexes **16**–**19** as photochemical WOCs. By using $[Ru(bpy)_3]^{3+}$ as PS, and persulfate as a sacrificial electron acceptor [26], they found that a high TON of 579 and a high quantum efficiency of 17% were found for **16**, which set a new record for visible light-driven water oxidation in homogeneous systems, while **17**–**19** showed similar activities (TON = 218–251 and TOF = 18.8–20.0), and **20** displayed a much lower activity (TON = 74 and TOF = 5.3) due to its instability. However, WOC **17** was reported to exhibit a TOF of >300 s^{-1} for water oxidation when using $Ce(NH_4)_2(NO_3)_6$ as the oxidant under acidic conditions, which is moderately comparable with the reaction rate of 100–400 s^{-1} of the oxygen-evolving complex of photosystem II in vivo [29]. It should be pointed out that light-driven water oxidation performance are still far less than that of chemically activated water oxidation performance. As a result, WOCs are usually evaluated and screened by chemical oxidation at first stage. For example, Thummel and Fujita and their coworkers have studied the effects of pendent basic nitrogen atoms in complexes **22** and **23** on their water oxidation and the proton reduction properties by using $(NH_4)_2[Ce(NO_3)_6]$ as sacrificial chemical oxidant. Proximal nitrogen-containing **22** was found to exhibit catalytic activity toward proton reduction but not toward water oxidation, while the geometric isomer, distal nitrogen-containing **23** exhibited the opposite behavior [30]. TON and initial rate values were reported to be only 1 and 1.1×10^{-3} s^{-1} for **22**, but 3200 and 1.8×10^{-2} s^{-1} for **23**, respectively. The TON value exhibited by **23**, compares favorably with a TON value of 460 for parent Ru complex $[Ru(tpy)(bpy)(H_2O)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine). It is noteworthy that the catalytic activity of **22** was suppressed by the addition of 10 equiv NaCl or even trace amounts of MeCN. Irrespective of relatively accessible highly oxidized Ru^{VI} state at a low potential, **22** exhibited poor water oxidation properties when Ce^{4+} was used, which was ascribed by authors to be catalyst decomposition as evidenced from the carbon dioxide detected during catalysis runs. Tanaka et al. have observed that cyclometalate Ru(II) complex **24** underwent geometrical transformation to **25** as irradiated under visible light at $\lambda > 420$ nm, and these two complexes acted as WOCs both chemically and electrochemically [31]. 10 nM of complexes **24** and **25** were used as WOCS catalyst in the presence of 16 mM Ce^{4+} in 0.1 M HNO3 exhibited TON values of 1200 and 3500, respectively. The cyclic voltammogram of aqueous solutions at pH 1.95 of these two complexes exhibited a redox couple at 0.31–0.33 V due to Ru^{II}/Ru^{III} and subsequent strong anodic currents at potentials more positive than +1.4 V vs. (SCE) are associated with water oxidation. **24** or **25** is the first example of a mononuclear cyclometalated ruthenium complex which behaves as a water oxidation catalyst (WOC) in electrochemical methods.