

Across the Board: Hiroshi Imahori

Hiroshi Imahori

Abstract: Abstract will be provided by the Editorial Office.

How to Achieve Efficient, Multi-electron Extraction from Water Photochemically?

Recently consumption of a large amount of fossil fuel has caused the environmental pollution as well as the greenhouse effect. We also have serious concern about exhaustion of the world's limited energy resources in near future because of continuous growing in population and economy, especially in developing countries. In these points of view, photovoltaics^[1] and artificial photosynthesis^[2] are highly desirable technologies to solve the issues as a result of substantially inexhaustible, clean nature of solar energy from the sun. In either case, core of the technologies is photoinduced charge separation in donor-acceptor systems, yielding donor radical cation and acceptor radical anion with the high abilities of respective oxidizing and reducing powers. Namely, electron and hole are extracted as photocurrent in photovoltaics, whereas oxidation and reduction reactions by the reactive species lead to the formation of respective oxidized and reduced products in natural photosynthesis.

Photovoltaics have been commercialized and expected to experience rapid growth in the future. However, at present the cost of production of electricity by photovoltaics is significantly higher than those by fossil fuel and nuclear power stations, hampering the widespread use. Meanwhile, artificial photosynthesis is still at the early stage of research and development, but it has attracted much attention recently in terms of merit of storable chemicals against transient-like electricity. In connection with mimicking parts of natural photosynthesis, there have been a number of photosynthetic model systems that successfully achieved excellent performances comparable to or even better than natural ones. As the next step there has emerged intense demand to create solar fuels that efficiently convert solar energy into chemicals.

Solar fuels can be defined as systems that extract electrons from ample water by visible light and donate the electrons to oxidized chemicals such as protons and carbon dioxide, generating useful reduced chemicals, hydrogen and formic acid, respectively. Thus, the oxidation of water molecules by visible light is essential toward the ultimate goal. In this regard, it is crucial to learn lesson from water oxidation mechanism in the oxygen-evolving complex (OEC) of Photosystem II. Recent

structural studies on the OEC by high-resolution X-ray crystallography have disclosed the distorted chair-like geometry of Mn_4CaO_5 cluster.^[3] However, considering five different oxidation states of the OEC, known as Kok cycle (S_0 , S_1 , S_2 , S_3 , and S_4) for successive four-electron water oxidation and the lack of relevant structural information including respective reactive water-derived species on the high-valent Mn metal, the water oxidation mechanism remains controversial. Moreover, recent rough estimation of the stepwise four-electron extraction from two water molecules indicated each period of 7.5 ms for the corresponding four-photon absorption.^[4] These requirements are severe obstacles toward the realization of solar fuels: i) water oxidation needs high oxidation potential more than 1.2 V vs. NHE; ii) highly reactive water-derived species on metals should survive to evolve oxygen at the time scale of 10^{-2} s in competition with other undesirable side reactions.

In this context there have been reported various OECs with different number (i.e., multi- and mononuclear complexes) of metals (Mn, Ru, Ir, Co, Cu, Fe). In particular, Sun^[5] and Tanaka^[6] developed ruthenium complexes **1** and **2** revealing the highest turnover numbers (TON: molar ratio of evolved oxygen with respect to the used catalyst) of 55400 and 33500 using oxidant $(\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]$ (CAN) and electrochemical oxidation, respectively (Figure 1). These values are close to or even comparable to the TON value in photosynthetic OEC. Importantly, they suggested that the dimeric structures of highly reactive water-derived species on the high-valent ruthenium metals ($\text{Ru}^{\text{V}}=\text{O}$ for **1** and $\text{Ru}^{\text{III}}-\text{O}^-$ for **2**) accelerate the formation of O-O bond to undergo four-electron oxidation of water to oxygen. Taking into account the successful development of highly active water oxidation catalysts, it is natural to combine such highly active dimeric water oxidation catalysts with photosensitizers to drive four-electron water oxidation photochemically.

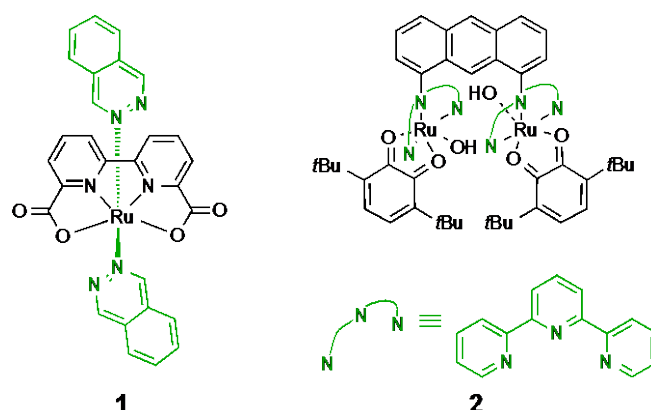
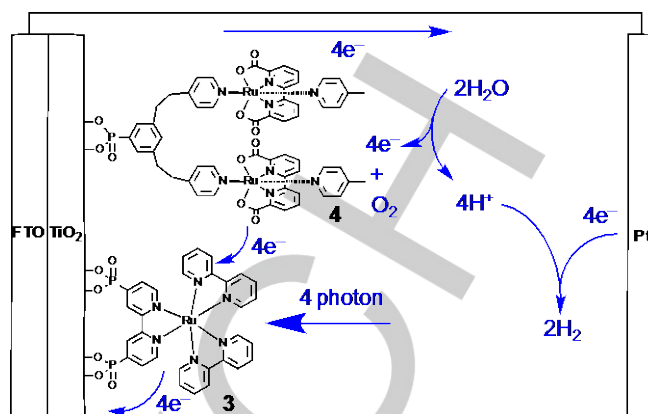


Figure 1. Molecular structures of highly efficient water oxidation catalysts **1** and **2**.

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Very recently, Gao and Sun et al. fabricated photoelectrochemical cell (PEC) with a TiO_2 -sintered fluoride-

doped tin oxide (FTO) electrode modified with both molecular photosensitizer **3** and binuclear ruthenium water oxidation catalyst **4** (Scheme 1).^[7] They expected that excitation of **3** by visible light would generate the energetic excited state, which is followed by electron injection to conduction band of the TiO₂. The resultant high oxidation power of **3**⁺ would drive intermolecular charge shift from **4** to **3**⁺ on the TiO₂ surface. Repeating this cycle would allow **3** to extract multiple electrons from **4**, yielding reactive oxo species on the Ru (Ru^V=O) and subsequent coupling within the dimeric structure. To confirm the concept, they also synthesized mono ruthenium water oxidation catalyst **5** as reference. The TiO₂ electrode was prepared by immersing it into a methanol solution of **3** and **4** with a molar ratio of 4:1. The cyclic voltammogram showed that the Ru^{II}/Ru^{III} redox couples of **4** appears at 0.68 V vs. NHE, the onset potentials (Ru^{III}-OH₂/Ru^{IV}-OH) of catalytic water oxidation at 1.10 V vs. NHE, and the redox peak of **3** at 1.40 V vs. NHE. Water-splitting performances of the three-electrode PECs with TiO₂/**3**+**4** and TiO₂/**3**+**5** were evaluated with an applied potential of 0.2 V vs. NHE in a 0.1 M Na₂SO₄ aqueous electrolyte solution under visible light illumination (Xenon lamp white-light source, 300 mW cm⁻²). Evolution of oxygen and hydrogen from the working and counter electrodes was visible. The Faradaic efficiencies of the generated oxygen (75%) and hydrogen (80%) of the TiO₂/**3**+**4** were considerably higher than those (68%, 72%) of the TiO₂/**3**+**5** under the same experimental conditions, implying the advantage of molecular binuclear catalyst over mononuclear one. Unfortunately, the photocatalytic performances were lower than those reported previously for their analogous work and the reason is not clear at this stage. Nevertheless, concept of coordinating molecular photosensitization and catalytic four-electron water oxidation on a semiconducting electrode is very interesting and highly promising for further improvement of the photocatalytic water oxidation performances.



Scheme 1. PEC with TiO₂ electrode assembled with photosensitizer **3** and binuclear ruthenium catalyst **4**.

Acknowledgements

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Keywords: photovoltaics • artificial photosynthesis • solar fuels • water oxidation • photoelectrochemical cell

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Hiroshi Imahori completed his doctorate in organic chemistry at Kyoto University. From 1990–1992, he was a post-doctoral fellow at the Salk Institute for Biological Studies, USA. In 1992, he became an Assistant Professor, ISIR, Osaka University and then moved to the Graduate School of Engineering, Osaka

University, as an Associate Professor. Since 2002, he has been a Professor of Chemistry, Graduate School of Engineering, Kyoto University. He received JSPS Prize

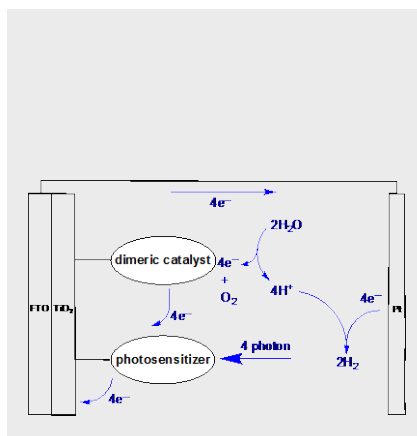
(2006), CSJ Award for Creative Work (2006), Osaka Science Prize (2007), and NISTEP Researcher Award (2007). His current interests involve artificial photosynthesis, organic solar cells, and organic functional materials.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

MINIREVIEW

Solar fuels: There are severe obstacles toward the realization of solar fuels: i) water oxidation needs high oxidation potential more than 1.2 V vs. NHE; ii) highly reactive water-derived species on metals should survive to evolve oxygen at the time scale of 10^{-2} s. This viewpoint highlights on recent progress on photocatalytic four-electron water oxidation by molecular photosensitizer and dimeric catalyst on semiconducting electrodes.

*Hiroshi Imahori****Page No. – Page No.****Title**
How to Achieve Efficient,
Multi-electron Extraction from
Water Photochemically?

Layout 2:

MINIREVIEW

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*Author(s), Corresponding Author(s)****Page No. – Page No.****Title**

Text for Table of Contents