Coordination Chemistry Reviews 377 (2018) 64–72

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Alternative route to bypass the bottle-neck of water oxidation: Two-electron oxidation of water catalyzed by earth-abundant metalloporphyrins

Fazalurahman Kuttassery [a], Siby Mathew [a], Sebastian Nybin Remello [b], Arun Thomas [a], Keito Sano [a], Yutaka Ohsaki [a], Yu Nabetani [c], Hiroshi Tachibana [a], Haruo Inoue [a,*]

[a] Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachiohji, Tokyo 192-0397, Japan
[b] Department of Applied Chemistry, Cochin University of Science and Technology, Kerala 682022, India
[c] Department of Applied Chemistry, University of Miyazaki, 1-1, Gakuen-Kibanadai-nishi, Miyazaki City, Miyazaki 889-2192, Japan

A R T I C L E I N F O

Article history:
Received 17 June 2018
Received in revised form 19 August 2018
Accepted 30 August 2018

Keywords:
Artificial photosynthesis
Water oxidation
Metalloporphyrin
Hydrogen peroxide

A B S T R A C T

Recent development on alternative route to bypass the bottle-neck of water oxidation, two-electron oxidation of water catalyzed by earth-abundant metalloporphyrins to form hydrogen peroxide, has been briefly reviewed. The three pioneering reports by Fujishima (Honda-Fujishima effect), Meyer (chemical oxidation of water), and Lehn (photochemical reduction of CO_2) triggered the extensive studies on artificial photosynthesis to have been forming the modern history of artificial photosynthesis. The current situation, especially for artificial photosynthesis by molecular catalysts, however, has faced with bottleneck subject of photon-flux-density problem of sun light radiation. In this review article, three milestones in the modern history of artificial photosynthesis, photon-flux-density problem as the bottleneck subject in water oxidation, crucial viewpoint of renewable energy factor (REF) in designing artificial photosynthesis even in fundamental stage of studies are explained. Several approaches to minimize the energy cost in REF for molecular catalysts such as utilization of earth-abundant elements and synthesis of molecular catalyst in water at ambient temperature were also introduced. Recent development of two-electron oxidation of water to form hydrogen peroxide, which would uncover the blind point of the bottleneck subject, would induce a game change in the methodologies of artificial photosynthesis.

Contents

1. Introduction

One of the most serious concerns for a sustainable globe should be that emission of carbon dioxide in huge amount is continuously increasing on energy demand by consumption of fossil fuels in ever

* Corresponding author.
E-mail address: inoue-haruo@tmu.ac.jp (H. Inoue).

https://doi.org/10.1016/j.ccr.2018.08.027
0010-8545/

inexperienced rate in a global scale to actually affect even macroscopic environment in apparent steady state condition [1–4]. Science and technology, thus, face with the subject and challenge in constructing a sustainable energy system on globe. Creation of renewable energy with zero-emission will surely lead to the most promising sustainable society as well as a tentative mitigation and adaptation against CO_2 emission. Among the possible energy sources for the renewable system, sun light should be the most probable candidate to be utilized for a sustainable system [1–4]. Realization of artificial photosynthesis which converts solar energy into chemical energy with water as an electron donor is most promising approach together with photovoltaic methodology of solar cells [1]. One of the most crucial key points in artificial photosynthesis should be how the system could utilize electrons in water for the reductive chemical conversions such as hydrogen evolution and CO_2 fixation in the reduction terminal end of a series of photo-induced redox reactions [3,4]. Artificial photosynthesis has been learning, mimicking natural photosynthesis, and trying to exceed it even in limited functions [4]. It has been, thus, quite natural to follow the conceptual methodology of natural photosynthesis in utilizing electrons in water molecule, that is, oxygen evolution from water by four-electron oxidation either by electrochemical and/or catalytic reactions has been extensively studied since the pioneering works as the three milestones in the modern history of artificial photosynthesis starting at early 1970's and mid 1980's [5–7]. Among various approaches for artificial photosynthesis such as 1) biological modification [8], 2) semiconductor photocatalysis [9–15], 3) molecular catalysis [16–21], 4) system integration [22–25], the molecular catalyst approach may be still in questionable situation to swiftly be realized in practical scale due to "bottle neck subjects" in water oxidation in spite of remarkable progress in the field [4]. In this article, what is the bottle neck subject in water oxidation and how we could get through or bypass the subject by an alternative route of two-electron oxidation of water in place of the conventional approach of four-electron oxidation will be overviewed based on recent progress.

2. Three milestones in the modern history of artificial photosynthesis

In 1972, Fujishima and Honda reported a pioneering work on photo-induced splitting of water into hydrogen and oxygen [5]. Irradiation of TiO_2 with UV light in water caused oxygen evolution on TiO_2 and hydrogen evolution on the counter electrode [5]. The phenomenon was named as "Honda-Fujishima effect" to be recognized as the first milestone in the modern history of artificial photosynthesis, which triggered extensive studies with a huge impact

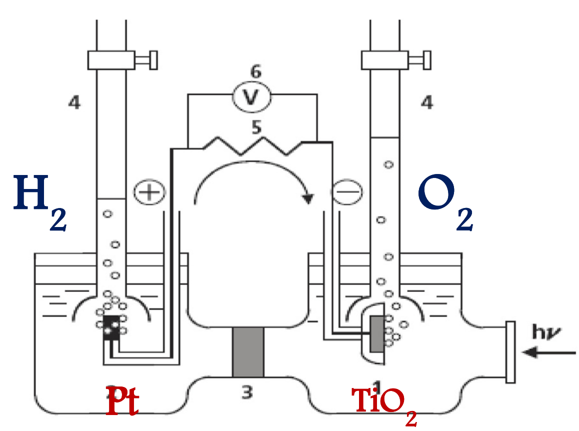
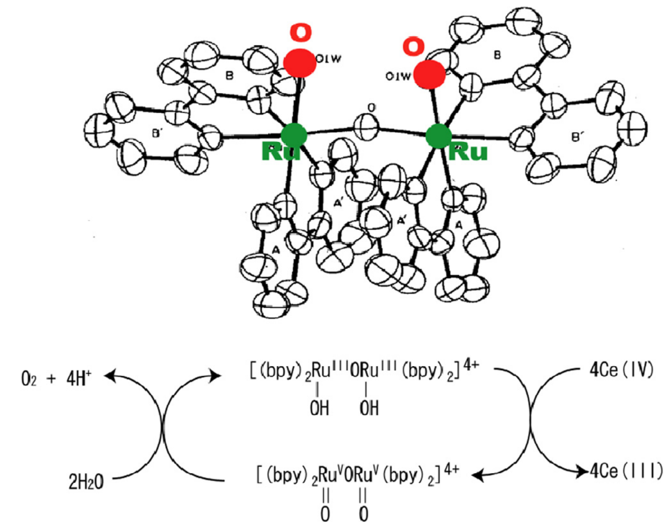
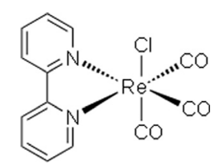


Fig. 1. Honda-Fujishima effect on photochemical splitting of water into hydrogen and dioxygen by the irradiation of TiO_2 with UV-light in water Ref. [5].



Scheme 1. Chemical oxidation of water into dioxygen catalyzed by dinuclear Ru-complex Ref. [6].



Scheme 2. Re-complex exhibiting a photochemical reduction of CO_2 into CO Ref. [7].

in scientific community. (Fig. 1) In early 1980's Meyer found the chemical oxidation of water molecule to evolve oxygen molecule catalyzed by di-nuclear Ru complex as the first example of water oxidation by molecular catalyst, which is recognized as the second milestone of artificial photosynthesis (Scheme 1) [6]. The third mile stone was put on the report by Lehn et al. for the photochemical reduction of CO_2 into CO catalyzed by Re complex (Scheme 2) [7]. Until the middle of 1980's the three pioneering reports had appeared as an apparently complete set of fundamental processes in artificial photosynthesis, affording a strong expectation against a realization of artificial photosynthesis in a short period. The situation was, however, not so straightforward and there still be bottle neck subjects to be resolved as described below.

3. How can we get electrons from water? Photon-flux-density problem as the bottle neck subject in water oxidation

What is the reason why artificial photosynthesis has not been realized soon after the pioneering works as the three milestones? In fact, there have been "a blind point" which has not been recognized so far. The "photon-flux-density problem" of sun light radiation had long been the blind spot before the definition of the concept which was postulated by Inoue et al. [4,26].

The essence of the concept is summarized as follows. When a molecule is excited to the electronically excited state by an absorption of photon, the electron donating ability and electron accepting one are both much enhanced compared with those in the ground state. The electron transfer from HOMO to an appropriate electron acceptor, or the electron transfer to LUMO from an appropriate electron donor ordinarily proceeds by one-electron transfer. A molecule can absorb only one photon upon collision against a photon under ordinary light intensity such as sun light radiation, being