



# Artificial photosynthesis for production of hydrogen peroxide and its fuel cells☆



Shunichi Fukuzumi

Department of Material and Life Science, Graduate School of Engineering, ALCA and SENTAN, Japan Science and Technology Agency (JST), Osaka University, Suita, Osaka 565-0871, Japan  
 Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea  
 Faculty of Science and Technology, Meijo University and ALCA and SENTAN, Japan Science and Technology Agency (JST), Tempaku, Nagoya, Aichi 468-8502, Japan

## ARTICLE INFO

### Article history:

Received 5 May 2015

Received in revised form 21 August 2015

Accepted 29 August 2015

Available online 10 September 2015

### Keywords:

Artificial photosynthesis

Solar fuel

Hydrogen peroxide

Fuel cells

## ABSTRACT

The reducing power released from photosystem I (PSI) via ferredoxin enables the reduction of  $\text{NADP}^+$  to  $\text{NADPH}$ , which is essential in the Calvin–Benson cycle to make sugars in photosynthesis. Alternatively, PSI can reduce  $\text{O}_2$  to produce hydrogen peroxide as a fuel. This article describes the artificial version of the photocatalytic production of hydrogen peroxide from water and  $\text{O}_2$  using solar energy. Hydrogen peroxide is used as a fuel in hydrogen peroxide fuel cells to make electricity. The combination of the photocatalytic  $\text{H}_2\text{O}_2$  production from water and  $\text{O}_2$  using solar energy with one-compartment  $\text{H}_2\text{O}_2$  fuel cells provides on-site production and usage of  $\text{H}_2\text{O}_2$  as a more useful and promising solar fuel than hydrogen. This article is part of a Special Issue entitled Biodesign for Bioenergetics – The design and engineering of electronic transfer cofactors, proteins and protein networks, edited by Ronald L. Koder and J.L. Ross Anderson.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Nature has optimized solar energy conversion within finely tuned molecular systems called photosynthetic reaction center proteins (RCs), in which efficient charge separation occurs with a high quantum efficiency to attain long-lived charge-separated state in photosystem I (PSI) and photosystem II (PSII) [1–4]. Photons absorbed by PSII are used to oxidize water in the oxygen-evolving complex (OEC) connected to PSII. The pH gradient formed over the thylakoid membrane during light-driven electron transport through PSII and PSI is concomitantly utilized by the ATP synthase (ATPase) for ATP formation [1–4]. The reducing power released from PSI via PSII by water oxidation enables the reduction of  $\text{NADP}^+$  to  $\text{NADPH}$  by which  $\text{CO}_2$  is reduced in the well-known Calvin–Benson cycle [1–4]. Alternatively, PSI can reduce various electron acceptors [5–8] including dioxygen ( $\text{O}_2$ ) in the Mehler reaction to produce hydrogen peroxide via disproportionation of superoxide anion [9,10]. The electron flow from the photosynthetic electron transport chain to molecular oxygen in the Mehler reaction can eliminate the excess of light energy, thus preventing the electron transport chain from photoinhibition [11–18]. Under normal functional conditions the reduction of molecular oxygen may represent about 5–10% of the total photosynthetic electron flow in C3 plants, however it can increase to 30% and even higher under stress conditions [19–21]. Mitochondria also produces  $\text{H}_2\text{O}_2$ , but at a rate approximately 20 times

slower in the light, indicating the potential importance of the Mehler reaction to the cellular level of  $\text{H}_2\text{O}_2$  [22]. It is now widely accepted that  $\text{H}_2\text{O}_2$  is utilized in metabolic regulation in ways similar to diffusible gases such as NO, CO, or  $\text{H}_2\text{S}$  [23–26].

Because of the large amount of energy released in the dismutation of hydrogen peroxide to water and dioxygen (Eq. (1):  $\Delta G^0 = -100$  kJ/mol) [27–29], it has become a powerful fuel material in the use of rocket propulsion [30–34] and micromotors [35–37].



Whole cells of microalgae or chloroplasts have been utilized for hydrogen peroxide production, exhibiting a variable efficiency depending on the origin of the photosynthetic membranes used as photocatalyst [38,39].

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) has recently received ever increasing attention as an alternative solar fuel to hydrogen. When  $\text{H}_2\text{O}_2$ , which contains two atoms of hydrogen and two atoms of oxygen, is used as a fuel, the only byproducts are steam, oxygen and heat with zero emissions of greenhouse gases. In contrast to gaseous hydrogen, hydrogen peroxide is a liquid, with low concentration (up to 10%) aqueous solutions used for bleaching hair, teeth, wood pulp and other products. High concentration (over 80%) aqueous solutions are generally used for a fuel. Hydrogen peroxide as a liquid form can also be easily transported over long distances using tankers, trucks and trains. Hydrogen peroxide can also be easily stored using a hydrogen peroxide fuel infrastructure, which would be similar to the current gasoline infrastructure. In contrast to hydrogen fuel cells, hydrogen peroxide fuel cells can operate with the absence of dioxygen environment, such as outer space and underwater

☆ This article is part of a Special Issue entitled Biodesign for Bioenergetics – the design and engineering of electronic transfer cofactors, proteins and protein networks, edited by Ronald L. Koder and J.L. Ross Anderson.

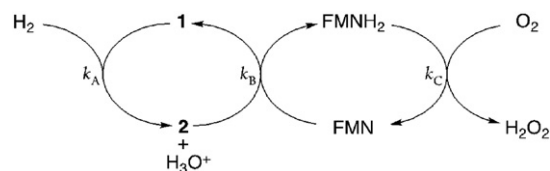
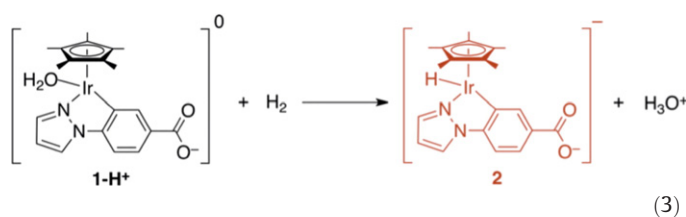
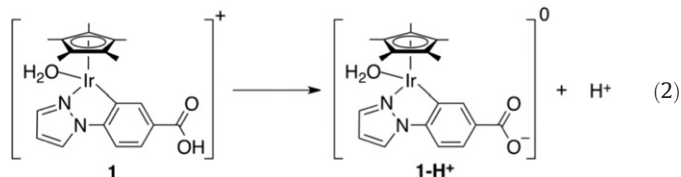
E-mail address: [fukuzumi@chem.eng.osaka-u.ac.jp](mailto:fukuzumi@chem.eng.osaka-u.ac.jp).

conditions without membranes and the use of hydrogen peroxide instead of  $O_2$  as an oxidant can substantially increase the theoretical voltage of fuel cells and thus improve cell performance [40,41]. Hydrogen peroxide is currently produced in industry by an anthraquinone (AQ) process, in which Pd-catalyzed hydrogenation of AQ with  $H_2$  produces anthrahydroquinone ( $H_2AQ$ ) and subsequent oxidation of  $H_2AQ$  by  $O_2$  yields  $H_2O_2$  [42,43]. The AO process is successfully used to produce most of the world's  $H_2O_2$  because it avoids explosive  $H_2/O_2$  gas mixture. However, the AO process suffers from several drawbacks, such as use of complex and toxic solvent system, periodic replacement of catalysts due to deactivation of catalysts, requirements of energy intensive processes for the removal of organic impurities. Transportation of  $H_2O_2$  creates additional safety concerns because concentrated  $H_2O_2$  can be explosive if it violently decomposes with metal catalysts. The high capital investment and operating costs for the AO process economically have precluded producing  $H_2O_2$  on-site at the end users facility. Thus, it is highly desired to produce hydrogen peroxide by a one-step process from  $H_2$  and  $O_2$  or more ideally from  $H_2O$  and  $O_2$  as observed in natural photosynthesis (vide supra). This review focuses on the recent development of direct synthesis of  $H_2O_2$  and artificial photosynthesis for production of hydrogen peroxide using solar energy and also its fuel cells to make electricity.

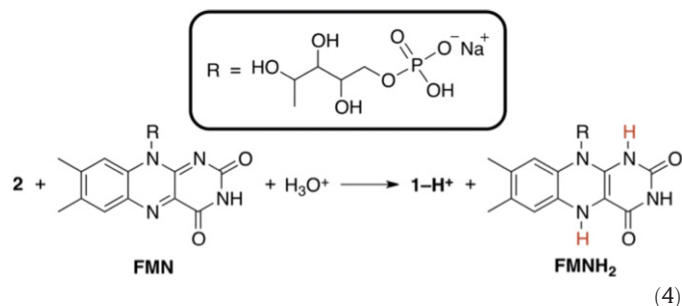
## 2. Direct synthesis of $H_2O_2$

Extensive efforts have so far been devoted to develop direct synthesis of  $H_2O_2$  from  $H_2$  and  $O_2$  using heterogeneous catalysts [44–47]. The major problem associated with the direct synthesis of hydrogen peroxide using heterogeneous catalysts comes from the limited selectivity of hydrogen usage due to undesired reactions such as formation of  $H_2O$ , decomposition of  $H_2O_2$ , and hydrogenation of  $H_2O_2$  [44–47]. In addition, it has been quite difficult to elucidate the heterogeneous catalytic mechanism as compared with the homogeneous catalytic mechanism, in which intermediates can be detected. The first direct synthesis of  $H_2O_2$  from  $H_2$  and  $O_2$  in a homogeneous system was reported by using a water-soluble iridium aqua complex  $[Ir^{III}(Cp^*)(4-(1H\text{-pyrazol-1-yl})K^N^2)\text{benzoic acid-}K^C^3)(H_2O)_2]_2SO_4$  ( $[1]_2SO_4$ ) and flavin mononucleotide (FMN) in water [48].

The carboxylic acid group in **1** is deprotonated to give the carboxylate form,  $1-H^+$  at pH 6.0 [Eq. (1)] [49,50].  $1-H^+$  reacts with  $H_2$  to produce the hydride complex (**2**) [Eq. (2)] [49,50]. **2** can reduce FMN to  $FMNH_2$  at pH 6.0 [Eq. (3)].  $FMNH_2$  is well known to be oxidized by  $O_2$  to regenerate FMN, accompanied by formation of  $H_2O_2$  [Eq. (4)] [51,52]. The overall catalytic cycle for the direct selective synthesis of  $H_2O_2$  from  $H_2$  and  $O_2$  with **1** and FMN is given by Scheme 1 [48]. The reduction of  $H_2O_2$  to  $H_2O$  by  $H_2$  was also catalyzed by **1** [48]. However, the reduction of  $H_2O_2$  was retarded by the presence of  $Sc^{3+}$ . Thus, the inhibition of further hydrogenation of  $H_2O_2$  was accomplished by the presence of strong acid such as  $Sc^{3+}$ , because  $H_2O_2$  is known to be stabilized by  $Sc^{3+}$  [53]. When **1** (1  $\mu M$ ) and FMN (50  $\mu M$ ) were used, TON based on **1** reached 847 for 4 h [48].

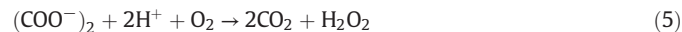


**Scheme 1.** Catalytic cycle for production of  $H_2O_2$  from  $H_2$  and  $O_2$  with a water-soluble iridium aqua complex (**1**) and FMN in water.



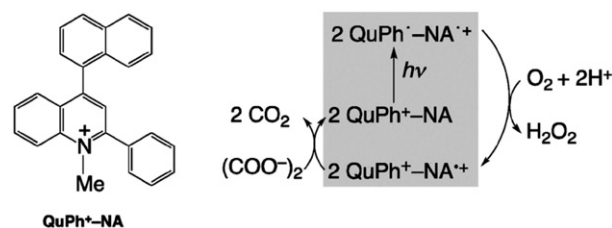
## 3. Photocatalytic reduction of $O_2$ to $H_2O_2$

Oxalic acid is used as a reductant for the two-electron reduction of  $O_2$  to produce  $H_2O_2$  in the enzymatic active center of oxalate oxidase [54–57]. Oxalate oxidase catalyzes the oxidation of oxalate and reduction of  $O_2$  to  $H_2O_2$  to produce two moles of carbon dioxide [Eq. (5)] [54–57]. Oxalate ion used as the reductant in Eq. (5) is produced in a



metabolic system during decomposition of glucose, which is produced from carbon dioxide and water by photosynthesis of plants. Thus, oxalic acid can be regarded as a carbon neutral reductant, although  $CO_2$  is emitted after reaction [Eq. (5)]. Oxalate can be found in the soil and leaves of various vegetables at a high content of ~1 wt.% [58].

Production of hydrogen peroxide from oxalate was made possible by using 2-phenyl-4-(1-naphthyl)quinolinium ion ( $QuPh^+-NA$ ) as an organic photocatalyst as shown in Scheme 2 [59,60]. Upon photoirradiation of  $QuPh^+-NA$ , intramolecular electron transfer occurs from the NA moiety to the singlet excited state of the  $QuPh^+$  moiety to produce the electron-transfer state ( $QuPh^+-NA^{\bullet+}$ ), which forms the  $\pi$ -dimer radical cation with  $QuPh^+-NA$  [61,62]. The  $NA^{\bullet+}$  moiety of the  $\pi$ -dimer radical cation can oxidize oxalate dianion. The second-order rate constant of electron transfer from oxalate dianion to the  $NA^{\bullet+}$  moiety of the  $\pi$ -dimer radical cation was determined by monitoring transient absorption in laser flash photolysis experiments to be  $1.6 \times 10^8 M^{-1} s^{-1}$  in an acetonitrile-water mixed solution with water content of 10% [59]. The  $QuPh^{\bullet}$  moiety of  $\pi$ -dimer radical cation can reduce  $O_2$  to  $O_2^{\bullet-}$  which disproportionates with protons to produce



**Scheme 2.** Chemical structure of  $QuPh^+-NA$  and overall catalytic cycle for  $H_2O_2$  production.

Download English Version:

<https://daneshyari.com/en/article/1942095>

Download Persian Version:

<https://daneshyari.com/article/1942095>

[Daneshyari.com](https://daneshyari.com)