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Review

Recent progress in production and usage of hydrogen peroxide

Shunichi Fukuzumi^{a,b,*}, Yong-Min Lee^{a,c,#}, Wonwoo Nam^{a,\$}^a Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea^b Graduate School of Science and Engineering, Meijo University, Nagoya, Aichi 468-8502, Japan^c Research Institute for Basic Sciences, Ewha Womans University, Seoul 03760, Korea

ARTICLE INFO

Article history:

Received 22 December 2020

Accepted 22 January 2021

Available online 5 April 2021

Keywords:

Hydrogen peroxide production

Water oxidation

Dioxygen reduction

Photocatalytic oxygenation

Reaction kinetics and mechanism

ABSTRACT

Hydrogen peroxide has attracted increasing interest as an environmentally benign and green oxidant that can also be used as a solar fuel in fuel cells. This review focuses on recent progress in production of hydrogen peroxide by solar-light-driven oxidation of water by dioxygen and its usage as a green oxidant and fuel. The photocatalytic production of hydrogen peroxide is made possible by combining the 2e⁻ and 4e⁻ oxidation of water with the 2e⁻ reduction of dioxygen using solar energy. The catalytic control of the selectivity of the 2e⁻ vs. 4e⁻ oxidation of water is discussed together with the selectivity of the 2e⁻ vs. 4e⁻ reduction of dioxygen. The combination of the photocatalytic 2e⁻ oxidation of water and the 2e⁻ reduction of dioxygen provides the best efficiency because both processes afford hydrogen peroxide. The solar-light-driven hydrogen peroxide production by oxidation of water and by reduction of dioxygen is combined with the catalytic oxidation of substrates with hydrogen peroxides, in which dioxygen is used as the greenest oxidant.

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1. Introduction

Hydrogen peroxide (H₂O₂) is an environmentally benign oxidant, being widely used for pulp- and paper-bleaching [1,2], wastewater treatment [3–6], oxidation of substrates [7–14], and fuel in fuel cells [15–20]. H₂O₂ is currently manufactured mainly by the anthraquinone process, in which an anthraquinone (such as 2-ethylanthraquinone or the 2-amyl derivative) is reduced by hydrogen (H₂) to the corresponding anthrahydroquinone using a palladium catalyst [21–23]. The anthrahydroquinone then undergoes autoxidation by dioxygen (O₂) to generate H₂O₂, accompanied by re-production of the anthraquinone. The high cost of the anthraquinone process resulting from recycling of the extraction solvents, the hydrogenation

catalyst and the expensive quinone has precluded the much wider use of H₂O₂ as a green oxidant and fuel. Direct synthesis of H₂O₂ from a mixture of H₂ and O₂ has provided an alternative route for the on-site generation [24–29]. However, H₂ and O₂ gases need to be diluted in high-pressure CO₂ or N₂ solution to prevent serious fire hazard, substantially lowering the yields of H₂O₂ [24–29]. On the other hand, electrochemical 2e⁻ reduction of O₂ has received increasing attention because of the research development on fuel cells [30–37]. A direct electrosynthesis strategy has recently been reported by delivering separate H₂ and O₂ streams to an anode and cathode parted by a porous solid electrolyte, wherein the electrochemically formed H⁺ and HO₂⁻ recombine to produce pure aqueous H₂O₂ solutions [38]. Because of the high cost of storage and transport of hydrogen

* Corresponding author. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

Corresponding author. E-mail: yomlee@ewha.ac.kr

\$ Corresponding author. E-mail: wwnam@ewha.ac.kr

This work was supported by the JSPS KAKENHI (16H02268) from MEXT, Japan and by the CRI (2012R1A3A2048842) and Basic Science Research Program (NRF-2020R11A1A01074630) through NRF of Korea.

DOI: 10.1016/S1872-2067(20)63767-6 | http://www.sciencedirect.com/journal/chinese-journal-of-catalysis | Chin. J. Catal., Vol. 42, No. 8, August 2021

gas, the electrolyzer type cell is preferred. However, higher cell voltages and electricity cost are required to drive the reaction to produce H_2O_2 [38]. Thus, the production of H_2O_2 by photocatalysis is a more sustainable process, because H_2O and O_2 are the earth-abundant and environmentally benign source materials and solar-light is used as the energy to drive the reaction between H_2O and O_2 [39–49]. This review focuses on recent mechanistic insights in solar-light-driven H_2O_2 production by oxidation of H_2O and by reduction of O_2 as well as the usage of H_2O_2 as a green oxidant and fuel.

2. $4e^-$ H_2O oxidation combined with $2e^-$ O_2 reduction

The first example of the photocatalytic H_2O_2 production by $4e^-$ H_2O oxidation combined with $2e^-$ O_2 reduction without hole scavengers was reported by combination of photoinduced electron transfer (ET) from the excited state of Ru(II) complex, $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+*}$ (* denotes the excited state and $4,7\text{-Me}_2\text{phen} = 4,7\text{-dimethyl-1,10-phenanthroline}$) to O_2 in the presence of an acid and the catalytic $4e^-$ oxidation of H_2O by $[\text{Ru}^{\text{III}}(4,7\text{-Me}_2\text{phen})_3]^{3+}$ with a H_2O oxidation catalyst (WOC) as shown in Scheme 1 [50]. ET from the photoexcited state of Ru(II) complex (Ru^{2+*}) to O_2 produces Ru(III) complex and $\text{O}_2^{\cdot-}$ species. $\text{O}_2^{\cdot-}$ is protonated in the presence of an acid to produce hydrogen peroxy radical ($\text{HO}_2^{\cdot}$), which disproportionates to yield H_2O_2 and O_2 [50]. A diversity of metal complexes and nanoparticles (NPs) is capable of catalyzing the $4e^-/4\text{H}^+$ H_2O oxidation by the Ru(II) photocatalyst to produce O_2 [51–61]. Hence, the net reaction of the photocatalytic $2e^-/2\text{H}^+$ O_2 reduction and the catalytic $4e^-/4\text{H}^+$ H_2O oxidation is the photocatalytic H_2O oxidation combined with O_2 reduction to produce H_2O_2 [50]. When $[(\text{Cp}^*)(\text{bpy})\text{Co}^{\text{III}}(\text{H}_2\text{O})]^{2+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$ and $\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) was used as a WOC with a photocatalyst, $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+}$, for the $2e^-/2\text{H}^+$ O_2 reduction in H_2O containing $\text{Sc}^{\text{III}}(\text{NO}_3)_3$, the quantum yield (Φ) of the photocatalytic H_2O_2 production at $\lambda = 450$ nm was determined as 37% [50]. The solar energy conversion efficiency of H_2O_2 production was determined using simulated solar-light (1 sun) to be 0.25% [50]. The solar-light-driven H_2O_2 production proceeds via photoinduced ET from the $\text{Ru}(\text{II})^*$ to O_2 to produce Ru(III) complex and $\text{O}_2^{\cdot-}$ species that binds to Sc^{3+} to produce $\text{O}_2^{\cdot-}\text{-Sc}^{3+}$ [62–64], which disproportionates in H_2O to yield H_2O_2 , while H_2O is oxidized to O_2 by four equivalents of Ru(III) photocatalyst with a WOC [50].

The photodriven production of H_2O_2 by oxidation of H_2O by O_2 was also achieved using NiFe_2O_4 NPs composed of

Scheme 1. Photodriven $4e^-$ H_2O oxidation combined with $2e^-$ O_2 reduction to produce H_2O_2 with WOC and $[\text{Ru}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ as a photocatalyst. Reproduced from Ref. [50] with permission from Royal Society of Chemistry (Copyright 2013).

earth-abundant metal ions as a WOC [65], $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ as a photocatalyst in H_2O containing $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ under visible-light illumination ($\lambda > 420$ nm) (Fig. 1(a)) [66]. NiFe_2O_4 NPs catalyst could be recycled by repeatedly adding Ru(II) complex to the reaction solution after cessation of production of H_2O_2 due to the decomposition of Ru(II) complex. The H_2O_2 concentration increased to reach 3.3 mM, indicating the high stability of NiFe_2O_4 NPs (Fig. 1(b)) [66]. The initial rate of H_2O_2 production with use of NiFe_2O_4 NPs with diameters of 120 and 91 nm was 22 and 33 times faster, respectively, as compared to that with use of NiFe_2O_4 NPs with a diameter of 1300 nm (Fig. 1(a)) [66]. Such an increase in catalytic reactivity occurs due to the increase in surface area of the WOC [66].

Heteropolynuclear cyanide metal complexes containing different metals such as $\text{Fe}_3[\text{Co}^{\text{III}}(\text{CN})_6]_2$ act as WOCs in the photocatalytic H_2O_2 production by oxidation of H_2O by O_2 with a photocatalyst, $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+}$, and a Lewis acid, $\text{Sc}^{\text{III}}(\text{NO}_3)_3$, under visible-light illumination ($\lambda > 420$ nm) in H_2O [67]. The catalytic reactivity was improved by changing the Fe-to-Co ratio in the $(\text{Fe}^{\text{II}}_x\text{Co}^{\text{II}}_{1-x})$ moiety of $(\text{Fe}^{\text{II}}_x\text{Co}^{\text{II}}_{1-x})_3[\text{Co}^{\text{III}}(\text{CN})_6]_2$ and the maximum catalytic reactivity was obtained with the Fe-to-Co ratio of 0.75 [67]. A larger Fe ratio in the $(\text{Fe}^{\text{II}}_x\text{Co}^{\text{II}}_{1-x})$ moiety would have more active sites for the H_2O oxidation catalysis, whereas a smaller Fe ratio would stabilize high-valent metals formed during the catalytic H_2O oxidation [67]. Such two opposite effects of Fe in H_2O oxidation catalysis was balanced to obtain the best ratio of Fe ($x = 0.75$) in $(\text{Fe}^{\text{II}}_x\text{Co}^{\text{II}}_{1-x})_3[\text{Co}^{\text{III}}(\text{CN})_6]_2$ for the photocatalytic H_2O_2 production [67].

Polymeric CN-bridged heteronuclear metal complexes, $\text{M}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$ ($\text{M}(\text{II}) = \text{Ni}(\text{II}), \text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$), act as bifunctional catalysts for both the $4e^-/4\text{H}^+$ H_2O oxidation to O_2 and the $2e^-/2\text{H}^+$ O_2 reduction to H_2O_2 in photocatalytic H_2O_2 production by oxidation of H_2O by O_2 [68]. The highest TON (turnover number) of 247 was obtained based on the monomer unit of $\text{Ni}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$ that was employed as a bifunction photocatalyst for the H_2O_2 production by oxidation of H_2O

Fig. 1. (a) Time profiles of photodriven H_2O_2 production under illumination ($\lambda > 420$ nm) of an O_2 -saturated aqueous solution containing $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ (0.20 mM), $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ (0.10 M) and NiFe_2O_4 NPs (0.17 g/L) with diameters of 1300 (black), 120 (blue) and 91 nm (red); (b) Time profile of photodriven H_2O_2 production under illumination ($\lambda > 420$ nm) of an O_2 -saturated aqueous solution containing Ru(II) (0.20 mM), $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ (0.10 M) and NiFe_2O_4 NPs (0.17 g/L). Ru(II) complex was added to the reaction solution at 50 and 100 h during the visible-light-driven H_2O_2 production. Reproduced from Ref. [66] with permission from Royal Society of Chemistry (Copyright 2015).

Scheme 2. Photocatalytic cycle of photodriven H_2O_2 production by oxidation of H_2O by O_2 with $\text{Ni}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$. Reproduced from Ref. [68] with permission from Royal Society of Chemistry (Copyright 2017).

by O_2 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1 v/v) containing $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ under illumination ($\lambda > 390 \text{ nm}$) [68]. No H_2O_2 was produced in pure CH_3OH , manifesting that water is the electron source of O_2 reduction [68]. The catalytic mechanism of the photocatalytic H_2O_2 production with $\text{Ni}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$ is proposed as shown in Scheme 2 [68], where ET from the photoexcited state of $\text{Ni}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$ to O_2 with Sc^{3+} to produce $[\text{Ni}(\text{II})[\text{Ru}(\text{III})(\text{CN})_4(\text{bpy})]]^+$ and $\text{O}_2^{\cdot-}-\text{Sc}^{3+}$ that disproportionates with H^+ to produce H_2O_2 [68]. Four equivalents of the $\text{Ru}(\text{III})$ moiety in $[\text{Ni}(\text{II})[\text{Ru}(\text{III})(\text{CN})_4(\text{bpy})]]^+$ oxidize water by the catalysis of the Ni moiety in $\text{Ni}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$ to evolve O_2 [68]. The dual function of $\text{M}(\text{II})[\text{Ru}(\text{II})(\text{CN})_4(\text{bpy})]$ as a single catalyst for the $4\text{e}^-/4\text{H}^+$ H_2O oxidation and the $2\text{e}^-/2\text{H}^+$ O_2 reduction provides an efficient integrated way to produce H_2O_2 by photocatalytic oxidation of H_2O by O_2 .

Hydrogen peroxide production by combining the catalytic $4\text{e}^-/4\text{H}^+$ H_2O oxidation to O_2 and the photocatalytic $2\text{e}^-/2\text{H}^+$ O_2 reduction to H_2O_2 using the same homogeneous solution described above inevitably competed with the further oxidation of H_2O_2 with a WOC to preclude production of H_2O_2 that is stable enough to obtain high concentrations ($> 10 \text{ mM}$). Hence, the photocatalytic H_2O_2 production by oxidation of H_2O by O_2 was performed with use of a two-compartment cell that consists of a semiconductor photocatalyst anode, which was separated by a Nafion membrane from a carbon cloth cathode in the presence of Ru complexes and $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ in an O_2 -saturated aqueous solution to obtain high concentrations of H_2O_2 in contrast to those with a one-compartment cell [69]. A schematic representation of such a two-compartment cell is shown in Fig. 2,

Fig. 2. A two-compartment cell employed for photocatalytic H_2O_2 production by combining the photocatalytic H_2O oxidation and the photocatalytic $2\text{e}^-/2\text{H}^+$ O_2 reduction under visible light illumination. Reproduced from Ref. [69] with permission from Royal Society of Chemistry (Copyright 2016).

Scheme 3. Photocatalytic water oxidation by O_2 to H_2O_2 by double photoexcitation. Reproduced from Ref. [69] with permission from Royal Society of Chemistry (Copyright 2016).

where WO_3 or BiVO_4 was employed as a photoanode for the photocatalytic H_2O oxidation [70–73] and a carbon mesh cathode was used for the $2\text{e}^-/2\text{H}^+$ O_2 reduction to H_2O_2 with a Ru complex [69]. The best performance was obtained when $[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$ ($(\text{MeO})_2\text{bpy} = 4,4'$ -dimethoxy-2,2'-bipyridine) was used as a photocatalyst for the $2\text{e}^-/2\text{H}^+$ O_2 reduction in an O_2 -saturated H_2O containing $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ (0.10 M) employing the carbon mesh cathode and the BiVO_4 photoanode for the photocatalytic H_2O_2 production by the H_2O oxidation by O_2 [69].

The mechanism of visible-light-driven H_2O_2 production by the catalytic H_2O oxidation by O_2 in the two-compartment cell is shown in Scheme 3 [69], where ET from photoexcited state of $\text{Ru}(\text{II})$ complex ($[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$) to O_2 with Sc^{3+} occurs to produce $\text{Ru}(\text{III})$ complex and $\text{O}_2^{\cdot-}-\text{Sc}^{3+}$ species [62–64] that disproportionates with H^+ to produce H_2O_2 in competition of back ET from $\text{O}_2^{\cdot-}-\text{Sc}^{3+}$ species to $\text{Ru}(\text{III})$ complex [50]. The photoexcitation of BiVO_4 results in generation of holes and electrons, which oxidize H_2O to O_2 and reduce $\text{Ru}(\text{III})$ to $\text{Ru}(\text{II})$, respectively [69].

The solar energy conversion efficiency in the solar-light-driven H_2O_2 production by oxidation of H_2O by O_2 using a two-compartment cell was much improved by employing monoclinic bismuth vanadate (BiVO_4), which was modified with metal oxide(hydroxide) ($\text{M}=\text{O}(\text{OH})$, $\text{M} = \text{Fe}, \text{Ni}$) as a photoanode [74–76] and a cobalt chlorin complex adsorbed on carbon paper ($\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$) as an efficient and selective catalyst for the $2\text{e}^-/2\text{H}^+$ reduction of O_2 [77,78] (Scheme 4) [79]. The best solar-to- H_2O_2 energy conversion efficiency was obtained as 6.6% and 0.89% under 0.05 sun and 1 sun irradiation,

Scheme 4. Solar-light-driven H_2O_2 production with $\text{FeO}(\text{OH})/\text{BiVO}_4/\text{FTO}$ photoanode and $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$ cathode in water or seawater under simulated 1 sun (AM 1.5G) irradiation. Reproduced from Ref. [79] with permission from American Chemical Society (Copyright 2016).

respectively [79]. These values are much larger than that of switchgrass (0.2%), which has been considered more recently as a biomass crop for ethanol and butanol (i.e., biomass fuel) [80].

Due to the global shortage of clean fresh water around the world, it is highly desirable to use seawater instead of pure water for solar-light-driven H_2O_2 production as a solar fuel, because seawater is the earth's richest water source. More efficient solar-light-driven production of H_2O_2 by the H_2O oxidation by O_2 was made possible by using seawater rather than pure water and O_2 in the air with use of a two-compartment cell composed of $m\text{-WO}_3/\text{FTO}$ photoanode and $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$ cathode [81]. The rate of photocatalytic H_2O_2 production in seawater was markedly enhanced as compared with that in pure water. After 24 h simulated solar-light irradiation, the concentration of H_2O_2 produced in seawater increased up to 48 mM, which could be directly used to operate an H_2O_2 fuel cell [81]. The virtually the same enhancement of solar-light-driven H_2O_2 production was observed using an NaCl solution, in which the concentration of Cl^- was the same as that in the seawater [81]. The oxidation of Cl^- rather than H_2O by photogenerated hole upon photoexcitation of WO_3 occurred to produce chlorine (Cl_2), which was converted to HClO depending on the pH of the solution [82]. HClO decomposed to produce O_2 and Cl^- under simulated solar-light irradiation [83]. Thus, the solar-light-driven water oxidation is accelerated by Cl^- [81]. The solar energy conversion efficiency for the solar-light-driven H_2O_2 production in seawater was determined to be 0.55% under simulated 1 sun illumination [81].

TiO_2 was reported to photocatalyze the production of H_2O_2 by Au NP loading to yield H_2O_2 on a 10 mM level [84]. Au/TiO_2 exhibited an efficient photocatalytic activity to attain the quantum yield (ϕ = molecules produced/incident photons) of 13% at the light wavelength ($\lambda = 355 \pm 23$ nm) [84]. However, 4% ethanol was necessary as a hole-scavenger for the photodriven production of H_2O_2 to proceed [84]. Aliphatic alcohols are frequently used as hole-scavengers for the photocatalytic H_2O_2 production by the $2e^-/2\text{H}^+$ O_2 reduction [85–88]. Graphitic carbon nitride (GCN), a metal-free polymeric semiconductor with a graphitic stacking structure of melem sheets also promotes selective $2e^-/2\text{H}^+$ O_2 reduction with ethanol to produce H_2O_2 [89–91]. However, the $g\text{-C}_3\text{N}_4$ catalyst is not capable of photocatalyzing H_2O_2 production by the water oxidation by O_2

[92], because the top of the valence band (VB) lies at approximately 1.4 V vs. NHE (normal hydrogen electrode) at pH 7 [93], which is insufficient for water oxidation (ca. 0.8 V) [94,95].

Incorporating aromatic diimides into graphitic carbon nitrides ($g\text{-C}_3\text{N}_4$) results in positive shifts of the oxidation and reduction potentials due to their high electron affinity [96]. Thus, incorporation of an electron deficient pyromellitic diimide (PDI) unit into the $g\text{-C}_3\text{N}_4$ network by thermal condensation (Scheme 5(a)) made it possible to act as a photocatalyst for H_2O_2 production by H_2O oxidation by O_2 without hole scavenger [97,98]. The $g\text{-C}_3\text{N}_4/\text{PDI}$ catalyst contains an electronic band structure capable of oxidizing H_2O and reducing O_2 as well [97,98]. Photoexcitation of the $g\text{-C}_3\text{N}_4/\text{PDI}$ catalyst at $\lambda < 470$ nm (A in Scheme 5(c)) results in formation of hole (h^+) and electron (e^-) pairs at 2,6- and 1,4-positions on the melem unit, respectively (B in Scheme 5(c)). The hole oxidizes H_2O , whereas the electron reduces O_2 to produce a superoxo radical (C in Scheme 5(c)). Rapid reduction of the radical by another e^- at the *para* position produces 1,4-endoperoxide species (D in Scheme 5(c)), which is readily transformed to H_2O_2 by the reaction with H^+ (Scheme 5(c)) [97,98]. The efficient formation of the endoperoxide species suppresses the e^-/H^+ or $4e^-/4\text{H}^+$ O_2 reduction, facilitating selective $2e^-/2\text{H}^+$ O_2 reduction to produce H_2O_2 [98]. Moreover, no decomposition of H_2O_2 occurred in the presence of $g\text{-C}_3\text{N}_4/\text{PDI}$ [98]. However, the amount of H_2O_2 produced after 48 h photoillumination was 30 μmol when the solar energy conversion efficiency was only 0.1% under simulated 1 sun irradiation, which should be much improved [97].

The solar energy conversion efficiency of photocatalytic H_2O_2 production with $g\text{-C}_3\text{N}_4/\text{PDI}$ was improved by hybridizing $g\text{-C}_3\text{N}_4/\text{PDI}$ with reduced graphene oxide (rGO) by simple hydrothermal-calcination sequence to attain 0.20% under simulated 1 sun illumination [98]. Strong interaction between $g\text{-C}_3\text{N}_4/\text{PDI}$ and rGO promotes photoinduced charge separation of h^+ and e^- [98]. The rGO acts as a trapping site for conduction band electron of the photoexcited $g\text{-C}_3\text{N}_4/\text{PDI}$ moiety as well as an active site promoting selective $2e^-/2\text{H}^+$ O_2 reduction, thus promoting efficient H_2O_2 production under simulated solar-light illumination [98].

Charge transfer (CT) interaction between electron donor (D) and electron acceptor (A) units of copolymers results in formation of D-A couples with low HOMO (highest occupied

Scheme 5. (a) Three-dimensional structure; (b) Electronic band structure of $g\text{-C}_3\text{N}_4/\text{PDI}$ (containing 51% PDI unit); (c) Photocatalytic cycle for H_2O_2 production from H_2O and O_2 with $g\text{-C}_3\text{N}_4/\text{PDI}$. Reproduced from Ref. [98] with permission from American Chemical Society (Copyright 2016).

molecular orbital) and LUMO (lowest unoccupied molecular orbital) gaps. The energy level hybridization by π -conjugation along the polymer chain and π -stacking between the chains forms a lower band-gap semiconductors with high conductivity to achieve efficient charge separation. High temperature and high pressure hydrothermal conditions were used to synthesize methylene-cross linked resorcinol-formaldehyde (RF) resins composed of a large number of quinoid forms of resorcinol acting as A, which are π -conjugated with inherent benzenoid forms of resorcinol as D [99]. The π -stacking of the benzenoid-quinoid D-A pairs leads to hybridization of the HOMO-LUMO levels, resulting in formation of semiconductors with low band-gaps. RF resins act as highly active D-A polymer photocatalysts to promote H_2O_2 production by oxidation of H_2O by O_2 using visible-light up to 700 nm [99]. Simulated solar-light illumination (1 sun) of the RF resin with O_2 in H_2O at barometric pressure produced H_2O_2 with the solar energy conversion efficiency of 0.5% [99].

In nature, water is oxidized in the photosystem II (PSII) to extract four electrons and four protons from two molecules of water, reducing the plastoquinone (PQ) in the quinone pool to produce plastoquinol (PQH_2) [100,101]. The overall solar-light-driven $4\text{e}^-/4\text{H}^+$ H_2O oxidation, accompanied by reduction of PQ, is given by Eq. (1), where PQ is reduced by H_2O to produce O_2 and PQH_2 [100,101].

Photodriven $4\text{e}^-/4\text{H}^+$ H_2O oxidation of by *p*-benzoquinone derivatives (X-Q), which is a potential functional mimic of PSII, was made possible by using a nonheme iron(II) complex, $[(\text{N4Py})\text{Fe}^{\text{II}}]^{2+}$ ($\text{N4Py} = N,N$ -bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine) as a WOC [Eq. (2)] [102]. Photoirradiation of an MeCN solution containing 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), $[(\text{N4Py})\text{Fe}^{\text{II}}]^{2+}$ and H_2O using a Xe lamp resulted in O_2 evolution with nearly 100% yield on the basis of the initial concentration of DDQ, while DDQ was reduced by H_2O to produce DDQH_2 [102]. The yield of O_2 evolution was reduced due to the oxidation of DDQH_2 by O_2 to produce H_2O_2 with the regeneration of DDQ in long light irradiation time [Eq. (3)] [102]. Other *p*-benzoquinone derivatives, such as *p*-benzoquinone, *p*-chloranil, toluquinone and duroquinone, with $[(\text{N4Py})\text{Fe}^{\text{II}}]^{2+}$ can also oxidize water to evolve O_2 under photoillumination [102].

The catalytic mechanism of the photodriven H_2O oxidation by X-Q with $[(\text{N4Py})\text{Fe}^{\text{II}}]^{2+}$ to evolve O_2 is shown in Scheme 6, where DDQ is employed as an oxidant [102]. Photoexcitation of DDQ results in formation of the triplet excited state ($^3\text{DDQ}^*$) via intersystem crossing from the singlet excited state ($^1\text{DDQ}^*$) [103,104]. $\text{Fe}(\text{II})$ species is oxidized by $^3\text{DDQ}^*$ via ET to produce $\text{Fe}(\text{III})$ and $\text{DDQ}^{\cdot-}$ species. The rate constant was determined by laser-induced transient absorption measurements to be $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is close to the diffusion-limited rate constant at 298 K. $\text{Fe}(\text{III})$ species produced by the photoinduced ET reacts with H_2O to generate the iron(III)-hydroxo ($[(\text{N4Py})\text{Fe}^{\text{III}}(\text{OH})]^{2+}$) complex and H^+ , whereas $\text{DDQ}^{\cdot-}$ is protonated to form $\text{DDQH}^{\cdot}$ (pathway a in Scheme 6). Iron(III)-hydroxo complex is further

Scheme 6. Proposed mechanism of the photocatalytic oxidation of H_2O by DDQ with $[(\text{N4Py})\text{Fe}^{\text{II}}]^{2+}$ to evolve O_2 . Reproduced from Ref. [102] with permission from American Chemical Society (Copyright 2019).

oxidized by $^3\text{DDQ}^*$ via ET to generate the iron(IV)-oxo [$\text{Fe}^{\text{IV}}(\text{O})$] complex and $\text{DDQH}^{\cdot}$ (pathway b in Scheme 6) [102]. The formation of iron(IV)-oxo was detected by the laser-induced transient absorption measurements ($\lambda_{\text{max}} = 690 \text{ nm}$) [102]. Then, ET from $\text{Fe}^{\text{IV}}(\text{O})$ to $^3\text{DDQ}^*$ occurs to generate the iron(V)-oxo [$\text{Fe}^{\text{V}}(\text{O})$] complex and $\text{DDQ}^{\cdot-}$. The rate constant of the photoinduced ET was determined to be $9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is also close to the diffusion-limited rate constant at 298 K (pathway c in Scheme 6) [102]. A nucleophilic attack of H_2O to $\text{Fe}^{\text{V}}(\text{O})$ generates the iron(III)-hydroperoxo [$\text{Fe}^{\text{III}}(\text{OOH})$] complex and H^+ (pathway d in Scheme 6) [102]. Iron(III)-hydroperoxo species is oxidized thermally by DDQ to produce the iron(III)-superoxo [$\text{Fe}^{\text{III}}(\text{O}_2^{\cdot-})$] complex and $\text{DDQH}^{\cdot}$ species (pathway e in Scheme 6), followed by O_2 release to regenerate iron(II) complex (pathway f in Scheme 6) [102]. It was confirmed that iron(III)-hydroperoxo was oxidized by DDQ thermally to evolve O_2 , when iron(III)-hydroperoxo complex was independently prepared by the oxidation of iron(II) complex by H_2O_2 [102]. DDQ can be replaced by other *p*-benzoquinone derivatives (X-Q) to achieve photocatalytic oxidation of H_2O by X-Q with iron(II) complex to evolve O_2 [102]. The combination of the photocatalytic $4\text{e}^-/4\text{H}^+$ H_2O oxidation by X-Q with iron(II) complex (i.e., $[(\text{N4Py})\text{Fe}^{\text{II}}]^{2+}$) and $2\text{e}^-/2\text{H}^+$ O_2 reduction by X-QH $_2$ would enhance the production of H_2O_2 by oxidation of H_2O by O_2 .

3. $2\text{e}^-/2\text{H}^+$ Oxidation of H_2O

In addition to the $4\text{e}^-/4\text{H}^+$ H_2O oxidation to evolve O_2 (the reverse reaction of the $4\text{e}^-/4\text{H}^+$ O_2 reduction), the $2\text{e}^-/2\text{H}^+$ H_2O oxidation affords H_2O_2 [Eq. (4)] [105,106]. The combination of the $2\text{e}^-/2\text{H}^+$ H_2O oxidation with the 2e^- reduction of 2H^+ [Eq. (5)] results in water splitting to produce H_2O_2 and H_2 [Eq. (6)] [106].

Fig. 3. (A) Photoanode and cathode for photoelectrochemical water splitting to H_2O_2 and H_2 . (B) Energy diagram of photoelectrocatalytic production of H_2O_2 and H_2 using a $\text{WO}_3/\text{BiVO}_4$ photoanode under solar-light illumination. Reproduced from Ref. [110] with permission from Royal Society of Chemistry (Copyright 2016).

The photoelectrochemical water splitting to H_2O_2 and H_2 has been achieved with use of a $\text{WO}_3/\text{BiVO}_4$ photoanode [107–109] under simulated solar-light illumination by applying potential much lower than that applied to the electrode in electrolysis (ca. > 0.4 V) (Fig. 3) [110]. H_2O_2 was produced only in the presence of KHCO_3 in H_2O and the maximum selectivity ($\eta(\text{H}_2\text{O}_2)$) for H_2O_2 production reached 54% in the presence of a high concentration (2.0 M) of HCO_3^- in H_2O at 5 °C, and the H_2O_2 concentration produced was 2.0 mM [110]. When KHCO_3 was replaced by other electrolytes, H_2O_2 was hardly produced [110]. Although the role of KHCO_3 for the photoelectrocatalytic production of H_2O_2 has yet to be well clarified, HCO_3^- oxidation in the holes of BiVO_4 may produce HCO_4^- and $\text{C}_2\text{O}_6^{2-}$, which act as an effective catalyst for the $2\text{e}^-/2\text{H}^+$ H_2O oxidation [107]. The Faraday efficiency of photoelectrocatalytic production of H_2O_2 and O_2 reached 100% in the anode reaction, indicating that the oxidized products of H_2O were only H_2O_2 and O_2 [110]. The maximum $\eta(\text{H}_2\text{O}_2)$ value was improved to 73% by using an Sb-modified anode containing mixed metal oxides such as $\text{CuSbO}_x/\text{FTO}$ and $\text{InSbO}_x/\text{FTO}$ [111]. The TON based on the number of loaded metal oxides exceeded 82,000 [111]. The H_2 gas was evolved as a reductive product of protons in Eq. (2) on the Pt cathode with 100% Faraday efficiency [110].

Bi_2WO_6 is also used as a suitable electrode for H_2O_2 production by $2\text{e}^-/2\text{H}^+$ oxidation of H_2O . The rate of H_2O_2 production was optimized by Mo-doping and enlarged specific surface area [110]. The $\text{FTO}/\text{Bi}_2\text{WO}_6:\text{Mo}$ electrode afforded the maximum Faraday efficiency of 79% at 3.2 V (vs. RHE), exhibiting good durability at least for 6 h electrolysis [110].

Combination of a $\text{WO}_3/\text{BiVO}_4$ photoanode with a HCO_3^- electrolyte for the $2\text{e}^-/2\text{H}^+$ oxidation of H_2O and an Au cathode for the $2\text{e}^-/2\text{H}^+$ reduction of O_2 resulted in solar-light-driven production of H_2O_2 ($\eta_{\text{anode}}(\text{H}_2\text{O}_2) \approx 50\%$ and $\eta_{\text{cathode}}(\text{H}_2\text{O}_2) \approx 90\%$) without applied potential between the photoanode and cathode under simulated solar-light illumination when an Au-supported porous BiVO_4 sheet (Fig. 4) was employed as a photocatalyst [111]. A composite electrode ($\text{WO}_3/\text{BiVO}_4+\text{Au}$), which was supported by both porous $\text{WO}_3/\text{BiVO}_4$ and Au on a single FTO substrate, was prepared to achieve simultaneous H_2O_2 production by the $2\text{e}^-/2\text{H}^+$ H_2O oxidation combined with the $2\text{e}^-/2\text{H}^+$ O_2 reduction on a single photoelectrode substrate

Fig. 4. A photoelectrode system for production of H_2O_2 via the $2\text{e}^-/2\text{H}^+$ H_2O oxidation on a $\text{WO}_3/\text{BiVO}_4$ photoanode combined with the $2\text{e}^-/2\text{H}^+$ O_2 reduction on an Au cathode under solar-light illumination. Reproduced from Ref. [111] with permission from John WILEY and Sons (Copyright 2017).

(photocatalyst sheet) without separating anode and cathode solutions under simulated solar-light illumination (Fig. 5(A) – (C)) [111]. The $\text{WO}_3/\text{BiVO}_4$ electrode was obtained by a two-step process using the same procedure on half of an FTO substrate and the Au sheet was prepared by the same sputtering method on another half of an FTO substrate (Fig. 5(A) and 5(B)) [111]. H_2O_2 was produced under photoirradiation even on this composite electrode containing $\text{WO}_3/\text{BiVO}_4$ and Au on a single FTO substrate in an aqueous solution containing KHCO_3

Fig. 5. (A) Reaction diagram of photocatalytic production of H_2O_2 ; (B) Composite electrode supported $\text{WO}_3/\text{BiVO}_4$ and Au on a single FTO substrate; (C) Solar-light-driven production of H_2O_2 on the composite electrode under simulated solar-light illumination in H_2O containing KHCO_3 (2.0 M) at below 5 °C under O_2 and CO_2 bubbling with use of a petri dish as a cell; (D) Reaction diagram of photocatalytic production of H_2O_2 on an Au-supported BiVO_4 powder in H_2O containing KHCO_3 (2.0 M) under O_2 and CO_2 bubbling. Reproduced from Ref. [111] with permission from John WILEY and Sons (Copyright 2017).

(2.0 M). The concentration of H_2O_2 reached approximately 130 μM after 60 min light photoradiation [111]. The realization of H_2O_2 production by using $\text{WO}_3/\text{BiVO}_4$ with an Au electrode under solar-light illumination suggests that an ultimate simple system is made possible by oxidative and reductive H_2O_2 generation by using BiVO_4 photocatalyst powder with Au particles as a cocatalyst (Fig. 5(D)) [111]. In fact, H_2O_2 (ca. 220 μM for 60 min) was produced by using Au-supported BiVO_4 photocatalyst powder suspended in H_2O containing KHCO_3 (2.0 M) under simulated solar-light illumination [111]. A $\text{BiVO}_4/\text{WO}_3$ photoelectrode was modified with Al_2O_3 by a chemical vapor deposition (CVD) method and solar-light-driven production of H_2O_2 in H_2O containing KHCO_3 (2.0 M) was achieved by using the $\text{Al}_2\text{O}_3/\text{BiVO}_4/\text{WO}_3$ photoelectrode and a biomass-derived carbon cathode without applying any external bias potential to obtain Faraday efficiencies of 44% for the cathode and 60% for photoelectrode [112].

4. Hydrogen peroxide fuel cells

Hydrogen peroxide obtained by the photocatalytic oxidation of water or seawater by O_2 (vide supra) was used as a fuel in a one-compartment H_2O_2 fuel cell composed of a Prussian blue-structured polynuclear cyanide complex ($\text{Fe}^{\text{II}}_3[\text{Co}^{\text{III}}(\text{CN})_6]_2$) adsorbed on a carbon cloth (CP) cathode and a nickel mesh anode [17–20,113]. Such a membraneless one-compartment H_2O_2 fuel cell utilizes H_2O_2 for both oxidant and reductant to achieve a theoretical output potential of 1.09 V (Scheme 7), which is only slightly lower but comparable to that can be obtained from a hydrogen fuel cell (1.23 V) [15]. The reaction solution (pH 1.3) containing H_2O_2 (52 mM) in the $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$ cathode produced after photocatalytic $4\text{e}^-/4\text{H}^+$ H_2O oxidation with the $\text{FeO}(\text{OH})/\text{BiVO}_4/\text{FTO}$ photoanode and the $2\text{e}^-/2\text{H}^+$ O_2 reduction with $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$ cathode (Scheme 4) was transferred to an H_2O_2 fuel cell, which exhibited an open circuit potential and a maximum power density of 0.79 V and 2.0 mW cm^{-2} , respectively (Fig. 6) [79]. The conversion of chemical energy to electric energy using H_2O_2 as a solar fuel was achieved to obtain the solar-to-electricity conversion efficiency of the total system as 3.3%, because the energy conversion efficiency of the H_2O_2 fuel cell was ~50% [79].

It is desired to replace a Ni anode used for one-compartment H_2O_2 fuel cells because Ni is vulnerable to H_2O_2 . An anodic catalyst composed of carbon nanotubes (CNTs)

Scheme 7. A membraneless one-compartment H_2O_2 fuel cell in which the anode ($2\text{e}^-/2\text{H}^+$ H_2O_2 oxidation) and cathode ($2\text{e}^-/2\text{H}^+$ H_2O_2 reduction) reactions afford the output potential of 1.09 V. Reproduced from Ref. [113] with permission from Royal Society of Chemistry (Copyright 2015).

Fig. 6. Plots of I - V (blue) and I - P (red) of a one-compartment H_2O_2 fuel cell with a $\text{Fe}^{\text{II}}_3[\text{Co}^{\text{III}}(\text{CN})_6]_2$ /carbon cloth cathode and a Ni mesh anode. Performance tests were carried out in a pH 1.3 aqueous solution, which was transferred from the $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$ cathode cell of the two-compartment cells containing 52 mM of H_2O_2 produced by photocatalytic H_2O oxidation by O_2 (see also Scheme 4). Reproduced from Ref. [79] with permission from American Chemical Society (Copyright 2016).

and vitamin B_{12} ($\text{CNT}/\text{VitB}_{12}$) was reported to promote the H_2O_2 oxidation, improving the cell performance of a membraneless H_2O_2 fuel cell [114]. The open circuit voltage (OCV) and maximum power density of the 100 mM H_2O_2 fuel were determined to be $0.233 \pm 0.005 \text{ V}$ and $53.8 \pm 0.4 \mu\text{W cm}^{-2}$, respectively [114].

A metal-free conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was utilized as a cathodic catalyst for the $2\text{e}^-/2\text{H}^+$ H_2O_2 reduction to H_2O with a Ni anode to obtain open circuit potentials in the range of 0.5 to 0.6 V with power densities in the range of 0.20 to 0.30 mW cm^{-2} [115]. The H_2O_2 fuel cell performance would be improved by optimizing PEDOT formulations or by switching to other next generation conductive polymers capable of developing anodic catalysts that facilitate H_2O_2 oxidation, leading to a complete metal-free membraneless one-compartment H_2O_2 fuel cell [115].

A membraneless microfluidic fuel cell (MMFC) with a single stream in the cotton threads is shown in Fig. 7, where a capillary coupled with gravity forces is used to move the reactant solution transport through the cotton threads without any external pump [13]. The MMFC consists of a cover plate, Ni mesh adopted as an anode to catalyze H_2O_2 oxidation, and Prussian blue (PB)-coated CP employed as a cathode to catalyze H_2O_2 reduction [13]. The cover and supporting plates composed of poly(methyl methacrylate) (PMMA) are used to fix and support electrodes, respectively. Thirty cotton threads are placed in parallel on the electrodes to form a flow channel for the reactant. In this MMFC, fuel crossover or diffusion mixing between fuel and oxidant can be avoided [13]. The MMFC generated an open circuit potential of 0.66 V with a maximum power density of 5.5 mW cm^{-2} , which are larger than those of other H_2O_2 MMFCs reported previously [116–121]. The MMFC was applied to develop a self-powered H_2O_2 electrochemical sensor on the basis of the proposed fuel cell structure [13].

Fig. 7. Illustration of a H_2O_2 MMFC. Reproduced from Ref. [13] with permission from American Chemical Society (Copyright 2020).

5. Oxidation of organic substrates with photogenerated H_2O_2

Hydrogen peroxide has been widely used for selective oxidation of organic substrates with oxidation catalysts [7–14]. The rational development of a series of oxidation catalysts for direct C–H or C–C bond activation with H_2O_2 has now reached maturity for use in selective late-stage functionalization of organic compounds [122–128]. Because H_2O_2 can be produced from H_2O as a reductant and O_2 as an oxidant (vide supra), combination of photodriven production of H_2O_2 by oxidation of H_2O by O_2 with the thermal oxidation of organic substrates by H_2O_2 with a catalyst provides a cost effective method for selective photodriven oxidation of organic substrates using only H_2O and O_2 as an oxygen source and an oxidant, respectively.

Photocatalytic production of H_2O_2 by oxidation of H_2O by O_2 with $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ as a photocatalyst and $[(\text{Cp}^*)\text{Co}^{\text{III}}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ as a water oxidation catalyst was combined with the catalytic hydroxylation of benzene with H_2O_2 using $[(\text{Cp}^*)\text{Co}^{\text{III}}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ that acts not only as a WOC but also as a benzene hydroxylation catalyst to yield phenol with TON > 500 (Scheme 8) [129]. This TON is much larger than those reported for photocatalytic hydroxylation of benzene with O_2 using organic photocatalysts [130–132]. Photoexcitation of $\text{Ru}(\text{II})$ complex resulted in formation of Ru^{2+*} and ET from Ru^{2+*} to O_2 in the presence of $\text{Sc}^{\text{III}}(\text{NO}_3)_3$ to produce $\text{Ru}(\text{III})$ complex and $\text{O}_2^{\cdot-}\text{Sc}^{3+}$ species that disproportionates to produce H_2O_2 and O_2 in the presence of H^+ (Scheme 8, pathways (b) and (c)) [129]. $\text{Ru}(\text{III})$ complex is used as an oxidant to oxidize water with $[(\text{Cp}^*)\text{Co}^{\text{III}}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (Scheme 8, pathway (a)).

Phenol Production by benzene hydroxylation has also been achieved by combination of the catalytic benzene hydroxylation with H_2O_2 and photocatalytic H_2O_2 production by oxidation of H_2O by O_2 with use of a CN-bridged polynuclear $\text{Fe}(\text{II})$ – $\text{Ru}(\text{II})$ complex ($\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$), incorporated into mesoporous silica-alumina (sAl-MCM-41), $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$ @sAl-MCM-41, acting as a triple functional catalyst for benzene hydroxylation catalyst, WOC and a photocatalyst for the $2\text{e}^-/2\text{H}^+$ O_2 reduction to H_2O_2 [133]. The catalytic durability was significantly improved by the incorporation of $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$ into

Scheme 8. Proposed mechanism of photocatalytic hydroxylation of benzene by combining photodriven production of H_2O_2 via $4\text{e}^-/4\text{H}^+$ H_2O oxidation and $2\text{e}^-/2\text{H}^+$ O_2 reduction with benzene hydroxylation by H_2O_2 using $[\text{Ru}^{\text{II}}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ as a photocatalyst and $[(\text{Cp}^*)\text{Co}^{\text{III}}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ as a dual function catalyst for the $4\text{e}^-/4\text{H}^+$ oxidation of water and hydroxylation of benzene. Reproduced from Ref. [129] with permission from Royal Society of Chemistry (Copyright 2017).

sAl-MCM-41. Remarkably, the selectivity of product to phenol was higher than 99%, indicating that no over-oxidation products, such as *p*-benzoquinone, were produced [133]. The TON of the formation of phenol reached 2500 at 114 h photoirradiation [133].

The proposed catalytic mechanism of photodriven benzene hydroxylation by O_2 with $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$ @sAl-MCM-41 in MeCN containing H_2O is shown in Scheme 9 [133]. Photoexcitation of $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$ resulted in ET from $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]^*$ to O_2 with Sc^{3+} to form $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{III}}(\text{CN})_6]^+$ complex and $\text{O}_2^{\cdot-}\text{Sc}^{3+}$ species that disproportionates with H^+ to produce H_2O_2 and O_2 [50]. $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{III}}(\text{CN})_6]^+$, which exhibits high oxidizing ability ($E_{1/2} = 1.24$ V vs. SHE) [133], can produce phenol by oxidizing

Scheme 9. Coupling of photo- and thermal catalysis by $\text{Fe}^{\text{II}}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$ @sAl-MCM-41 for photocatalytic hydroxylation of benzene by O_2 with H_2O . Reproduced from Ref. [133] with permission from American Chemical Society (Copyright 2016).

Fig. 8. External bias-free, PEC H_2O_2 production by oxidation of H_2O by O_2 with use of an $\text{FeOOH}/\text{BiVO}_4/\text{CIGS}$ solar cell in tandem and CN/rGO film electrode under photoirradiation for chemo- and stereospecific conversion of ethylbenzene to obtain (*R*)-1-phenylethanol catalyzed by AaeUPO. Reproduced from Ref. [134] with permission from American Chemical Society (Copyright 2019).

the $\text{Fe}(\text{II})$ moiety to a high-valent iron species effective in both oxidation of water and hydroxylation of benzene with H_2O_2 [133].

The catalytic oxidation of organic substrates with H_2O_2 combined with the photocatalytic H_2O_2 production by oxidation of H_2O by O_2 provides a new strategy to achieve one-pot oxygenation of substrates using O_2 as the greenest oxidant and H_2O as the most environmentally benign oxygen source.

An unbiased photoelectrochemical (PEC) tandem cell composed of a $\text{FeOOH}/\text{BiVO}_4$ photoanode, a $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar absorber, and a graphitic carbon nitride/reduced graphene oxide hybrid cathode (Fig. 8) was developed to achieve photocatalytic stereoselective ethylbenzene hydroxylation to obtain (*R*)-1-phenylethanol with TONs larger than 4.3×10^4 , a TOF (turnover frequency) of 12.9 s^{-1} and high enantioselectivity ($ee > 99\%$) [134]. A sufficient photovoltage is generated by the solar absorber, producing H_2O_2 in situ by $2\text{e}^-/2\text{H}^+$ reduction of O_2 combined with $2\text{e}^-/2\text{H}^+$ oxidation of H_2O in the absence of external bias. As a counter electrode in the PEC tandem cell, graphitic carbon nitride (CN) and reduced graphene oxide (rGO) hybrid film was used as an effective cathode material for the $2\text{e}^-/2\text{H}^+$ reduction of O_2 using electrons extracted from water oxidation at the BiVO_4 photoanode [132]. In order to increase the electrochemical active surface area, rGO was used as a supporting layer for CN [135]. The recombinant peroxygenase from *Agrocye aegerita* (AaeUPO) catalyzed selectively the ethylbenzene hydroxylation with H_2O_2 to yield (*R*)-1-phenylethanol [134]. Thus, integration of unbiased PEC system with peroxygenases has been demonstrated to promote C-H oxyfunctionalization using solar-powered electrons extracted from H_2O .

6. Conclusion and perspective

Combination of $2\text{e}^-/2\text{H}^+$ reduction of O_2 with photodriven $4\text{e}^-/4\text{H}^+$ oxidation of H_2O resulted in photocatalytic H_2O_2 production by oxidation of H_2O by O_2 . A homogeneous photocatalytic system for photodriven production of H_2O_2 by oxidation of H_2O by O_2 is composed of a $\text{Ru}(\text{II})$ complex acting as a photo-redox catalyst for $2\text{e}^-/2\text{H}^+$ O_2 reduction to produce H_2O_2 and a $\text{Co}(\text{III})$ complex acting as a redox catalyst for $4\text{e}^-/4\text{H}^+$ H_2O oxi-

dation to evolve O_2 . Heterogeneous photocatalysts for water oxidation can also be used to be combined with a $\text{Co}(\text{III})$ chlorin complex for $2\text{e}^-/2\text{H}^+$ O_2 reduction to achieve photodriven production of H_2O_2 by oxidation of H_2O by O_2 . Both $2\text{e}^-/2\text{H}^+$ H_2O oxidation and $2\text{e}^-/2\text{H}^+$ O_2 reduction yield H_2O_2 simultaneously. Thus, simultaneous H_2O_2 production by the $2\text{e}^-/2\text{H}^+$ H_2O oxidation and the $2\text{e}^-/2\text{H}^+$ O_2 reduction has been achieved using a single photocatalyst sheet without separation of anode and cathode solutions under simulated solar-light illumination. H_2O_2 produced by photodriven H_2O oxidation by O_2 is used as a fuel in H_2O_2 fuel cells to obtain electricity. Solar-light-driven production of H_2O_2 by H_2O oxidation by O_2 is also combined with green oxidation of organic substrates with H_2O_2 when O_2 is used as the greenest oxidant and H_2O as the most environmentally benign oxygen source. The best solar-to- H_2O_2 energy conversion efficiency has so far been limited to 6.6% and 0.89% under 0.05 sun and 1 sun, respectively [79]. The further improvement of the efficiency of solar-light-driven production of H_2O_2 will be made by the combination of $2\text{e}^-/2\text{H}^+$ H_2O oxidation and $2\text{e}^-/2\text{H}^+$ O_2 reduction, facilitating the use of H_2O_2 as a solar fuel in fuel cells as well as a green oxidant.

Acknowledgments

The authors gratefully acknowledge the contributions of their collaborators and coworkers mentioned in the cited references.

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Graphical Abstract

Chin. J. Catal., 2021, 42: 1241–1252 doi: 10.1016/S1872-2067(20)63767-6

Recent progress in production and usage of hydrogen peroxide

Shunichi Fukuzumi*, Yong-Min Lee*, Wonwoo Nam*
Ewha Womans University, Korea; Meijo University, Japan

This review focuses on recent progress in solar-light-driven H_2O_2 production by oxidation of H_2O and by reduction of O_2 as well as the usage of H_2O_2 as a green oxidant and fuel.

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过氧化氢生产与利用的新进展

Shunichi Fukuzumi^{a,b,*}, Yong-Min Lee^{a,c,#}, Wonwoo Nam^{a,\$}

^a梨花女子大学化学与纳米科学系, 首尔, 韩国

^b美珠大学科学与工程研究生院, 名古屋, 日本

^c梨花女子大学基础科学研究院, 首尔, 韩国

摘要: 过氧化氢既可用作环境友好的绿色氧化剂, 也可用作燃料电池中的太阳能燃料, 因而受到越来越多的关注. 本文综述了太阳能驱动分子氧氧化水制备过氧化氢及其作为绿色氧化剂和燃料的研究进展. 利用太阳能将水的 $2e^-$ 和 $4e^-$ 氧化与分子氧的 $2e^-$ 还原相结合, 使光催化生产过氧化氢成为可能; 本文讨论了与 $2e^-$ 和 $4e^-$ 水氧化选择性及 $2e^-$ 和 $4e^-$ 氧还原选择性相关的催化反应控制. 由于光催化 $2e^-$ 氧化水和 $2e^-$ 还原分子氧的过程都产生过氧化氢, 因此该组合的催化效率较高. 太阳能光驱动水氧化及分子氧还原生产过氧化氢与过氧化氢催化氧化底物相结合, 在该过程中分子氧用作最环保的氧化剂.

关键词: 过氧化氢生产; 水氧化; 分子氧还原; 光催化氧化; 反应动力学与机理

收稿日期: 2020-12-22. 接受日期: 2021-01-22. 上网时间: 2021-04-05.

*通讯联系人. 电子信箱: fukuzumi@chem.eng.osaka-u.ac.jp

#通讯联系人. 电子信箱: yomlee@ewha.ac.kr

\$通讯联系人. 电子信箱: wwnam@ewha.ac.kr

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