Artificial Photosynthetic Systems for Production of Hydrogen

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The rapid consumption of fossil fuels has caused unacceptable environmental problems such as the greenhouse effect, which may lead to disastrous climatic consequences. Because fossil fuels are the products of long-term photosynthesis, it is highly desirable to develop artificial photosynthetic systems for the production of renewable and clean energy such as hydrogen. This article summarizes recent advances on studies of artificial photosynthetic systems for photocatalytic production of hydrogen with hydrogenases and their functional mimics including hybrids of natural and artificial components. Because it is highly desired to convert gaseous H₂ to an easily storable form, recent progress on storage of hydrogen as liquid or solid form has also been described in this article.

Introduction

Photosynthesis is an important biological process by which plants and some bacteria utilize solar energy to produce ATP and NADPH for fixation of CO₂ in the Calvin cycle [1]. The solar energy has been stored as fossil fuels, which were made through photosynthesis over a billion years. As the world population grows and the standard of living improves, the world's consumption rate of fossil fuels is also rapidly growing. The combustion of fossil fuels has already led to unacceptable levels of pollution of our environment by the release of the huge amount of CO₂, which has caused the green

house effect on the earth [2]. Thus, the sustainable production of solar fuels, such as H₂ from water, by artificial photosynthesis is a promising means to replace fossil fuels for long-term global energy requirements [2,3]. There has been much effort for development of artificial photosynthesis including hybrids of natural and artificial components [3-9], which is summarized in this article. 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 [1]. The Photosystem I RC protein (PSI) [10] has been combined with [NiFe]- and [FeFe]-hydrogenase enzymes [11,12] to drive H₂ production [8,9]. The hydrogenase enzymes have been replaced by Pt nanoclusters [8,9]. In addition, the RC protein has also been replaced by synthetic organic compounds, which undergo efficient charge separation with slow charge recombination [13]. Various hydrogenase functional mimics have been developed as efficient catalysts for H₂ production to replace Pt nanoclusters by more earth-abundant materials [14-18].

Because H₂ gas is explosive and its volumetric energy density is quite low, low-cost, energy-efficient storage of H₂ as a liquid or solid form is definitely needed for stationary and portable applications in the H₂-delivery infrastructure, which is also described in this article [19].

Biohybrids for H₂ production

Electrons produced by the water splitting Photosystem II (PSII) are transferred to the Photosystem I (PSI) and finally to ferredoxin (Fd) [1]. Fd serves as a reducing agent to generate NADPH primarily for autotrophic carbon dioxide fixation via the Calvin-Benson-Bassham (CBB) cycle [1]. Although NADPH is an indispensable reductant in living cells, it is not particularly useful as a source of stored bond energy for human activity. NADPH is the biological equivalent of H₂; both are oxygen-stable, and their

standard redox potentials are similar (the E^0 of the $\text{NADP}^+/\text{NADPH}$ couple at pH = 7 is -324mV, whereas the E^0 of the H^+/H_2 couple is -414 mV) [20,21]. Although, the hydrogenase and PSI are not physiological redox partners, H_2 production by the combination of PSI and hydrogenase is thermodynamically feasible. Okura and coworkers reported fusion of the PSI subunit PsaE from the cyanobacterium *Thermosynechococcus elongatus* with an O_2 -tolerant [NiFe] hydrogenase from *Ralstonia eutropha* H16 [22]. The hydrogenase-PSI complex displayed light-driven hydrogen production with ascorbate as an electron donor at a rate of $0.58 \mu\text{mol H}_2 (\text{mg chlorophyll})^{-1} \text{h}^{-1}$ [22,23].

Hydrogenase can be replaced by Pt nanoclusters for the photocatalytic hydrogen production with PSI [24]. PtNPs bind readily to native PSI as shown in Figure 1a. The size of the nanoparticles was estimated to be $3.0 \pm 0.2 \text{ nm}$ [25]. PtNPs form a complex with PSI in a 1.0 ± 0.2 Pt nanoparticle/PSI monomer; nearly 1:1 ratio. Cytochrome c_6 acts as the soluble mediator and ascorbate as a sacrificial electron donor, when visible-light-driven H_2 production occurs efficiently with the PSI/Pt nanoparticle biohybrids at a rate of $244 \mu\text{mol H}_2 (\text{mg chlorophyll})^{-1} \text{h}^{-1}$ [25]. Upon photoexcitation of PSI, photoinduced electron transfer occurs from the primary electron donor P700 (a dimer of chlorophyll molecules) through a series of protein-embedded donor/acceptor molecules including three [4Fe-4S] clusters, FX, FA, and FB, to the Pt nanoparticle (Figure 1b) [25]. A fully optimized PSI/molecular wire/Pt nanoparticle system with cross-linked plastocyanin (native electron donor protein to P700⁺) exhibited a higher H_2 production rate of $312 \mu\text{mol H}_2 (\text{mg chlorophyll})^{-1} \text{h}^{-1}$ [26,27].

Figure 1. (a) Photocatalysis of PSI/Pt nanoparticle complexes. (b) Schematic representation of the cofactors involved in sequential electron transfer in PSI. Cytochrome c₆ (shown) or plastocyanin are donors to P700⁺. A Pt nanoparticle is depicted in place of the native protein acceptors of PSI, either ferredoxin or flavodoxin.

[FeFe]-hydrogenase from *Clostridium acetobutylicum* (CaI) has also been combined with CdS nanorods (NRs) instead of PSI for photoinduced H₂ production using ascorbate as an electron donor with quantum yields (QY(H₂)) of up to 20% at a CaI:CdS NR molar ratio of 1:1, where QY(H₂) is defined as (H₂ molecules produced/photons absorbed) × (2 electrons/H₂ molecule) [28]. The CdS-CaI complexes are formed by binding of CdS NRs, which are capped with negatively charged surface ligands, with CaI as analogs of the electron-donating protein Fd [28]. Photoexcitation of CdS is followed by electron transfer from CdS to a distal iron-sulfur cluster followed by transport through a series of accessory iron-sulfur clusters to the active site of CaI in which two electrons are reduced to H₂, whereas holes are scavenged by the electron donor ascorbate (AscH⁻) [28,29] .

Inorganic photocatalysts for H₂ production

Both PSI and hydrogenases for photoinduced H₂ production described above can be replaced by artificial components, composed of a sacrificial electron donor, an inorganic photocatalyst, and a proton reduction catalyst, which have been extensively studied since late 1970s [30-32]. A typical homogeneous photocatalytic system for H₂ production using an inorganic photocatalyst is shown in Scheme 1, where photoinduced electron transfer from ascorbate to the excited state of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) occurs to produce [Ru(bpy)₃]⁺ as a primary photogenerated reductant, which is capable of reducing a cobalt complex cobalt(II) complex with 6-(bis(bis-2-pyridyl)-methoxymethane) pyridine pentadentate ligand with a fast rate (bimolecular rate constant $k = 5.7 (\pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [33]. For hydrogen generation, two one-electron photochemical reduction steps of the cobalt(III) complex are needed along with hydride formation and protonation [33].

Scheme 1. Photocatalytic cycle for H₂ production under visible light irradiation of the photolysis mixture containing [Ru(bpy)₃]²⁺, a cobalt(II) complex with 6-(bis(bis-2-pyridyl)-methoxymethane) pyridine pentadentate ligand (**1**), and ascorbic acid. Abbreviations: Ru(II) = [Ru(bpy)₃]²⁺, *Ru(II) = [Ru(bpy)₃]^{2+*}, Ru(I) = [Ru(bpy)₃]⁺, AscH⁻ = ascorbic acid, DHA = dehydroascorbic acid.

A high turnover number (TON = 6500) has been achieved for photocatalytic H₂ production using (4,4'-di-tert-butyl-2,2'-dipyridyl)-bis(2-phenylpyridine-(1H))-iridium(III) hexafluorophosphate [Ir(ppy)₂(dtbbpy)][PF₆] as a photocatalyst and triethanolamine (TEOA) as a sacrificial electron donor and a tetra-nickel-containing polyoxotungstate, Na₆K₄[Ni₄(H₂O)₂(PW₉O₃₄)₂] $\cdot$ 32H₂O (Na₆K₄-Ni₄P₂) as a noble metal-free molecular catalyst [34]. The excited state [Ir(ppy)₂(dtbbpy)]⁺* was both oxidatively and reductively quenched by Ni₄P₂ and TEOA, respectively [34]. Extensive stability studies (e.g., UV-vis absorption, FT-IR, mercury-poison test, dynamic light scattering (DLS) and transmission electron microscopy (TEM)) provided evidence that the Ni₄P₂ catalyst remains homogeneous and intact under turnover conditions [34].

How a photoinduced electron-transfer reaction of a photocatalyst (a one-electron process) leads to H₂ production (a two-electron process) has been clarified in [Ru(bpy)₃]²⁺-catalyzed light-driven H₂ production from ascorbic acid using [Rh^{III}(Cp*)(bpy)(H₂O)](SO₄) (Cp* = η^5 -C₅Me₅) and [Ir^{III}(Cp*)(H₂O)-(bpm)Ru^{II}(bpy)₂](SO₄)₂ (bpm=2,2'-bipyrimidine) as proton reduction catalysts [35]. The laser flash photolysis studies have revealed the photocatalytic mechanism as shown in Scheme 2 [35]. Photoinduced electron transfer from HA⁻ to [Ru(bpy)₃]²⁺* (a one-electron process) leads to the two-electron reduction of protons to produce H₂ by disproportionation of the one-electron-reduced species of [Rh^{III}(Cp*)(bpy)(H₂O)]²⁺ and [Ir^{III}(Cp*)(H₂O)-(bpm)Ru^{II}(bpy)₂]²⁺ to afford the two-electron-reduced metal complexes, which are protonated to give the metal hydride complexes. Hydrogen is produced by reactions of the metal hydride complexes with protons to regenerate the oxidized catalysts [35]. Thus, disproportionation of the one-electron-reduced metal complexes is responsible for the conversion from the one-electron process (photoinduced electron transfer) to the two-electron process (H₂ production).

Scheme 2. Photocatalytic H₂ evolution with metal complexes (M = Rh and Ir complexes) by a disproportionation mechanism.

Organic photocatalysts for H₂ production

The photocatalytic efficiency of H₂ evolution has been much improved by using organic donor-acceptor linked molecules with a long-lived electron-transfer state [36,37], which can inject electrons directly to hydrogen-evolution catalysts without an electron mediator upon photoexcitation of the donor-acceptor linked dyads instead of using inorganic photocatalysts [38,39]. A very high quantum yield (QY(H₂) = H₂ molecules produced/photons absorbed) × (2 electrons/H₂ molecule = 52%) and a high yield of H₂ (95%) based on an electron donor (NADH) have been achieved under photoirradiation of a deaerated phthalic acid buffer (pH 4.5, 50 mM) and acetonitrile (MeCN) [1:1 (v/v)] mixed solution containing 9-mesityl-10-methylacridinium ion (Acr⁺-Mes) (0.10 mM), NADH (1.0 mM) and poly(N-vinyl-2-pyrrolidone)-protected platinum nanocluster (Pt-PVP) (0.20 mg) at 298 K [39]. Upon photoexcitation of Acr⁺-Mes, the electron-transfer state (Acr[•]-Mes^{•+}) is formed and electron transfer from NADH to the Mes^{•+} moiety of Acr[•]-Mes^{•+} occurs rapidly to produce NADH^{•+} and Acr[•]-Mes (Scheme 3). NADH^{•+} deprotonates to produce NAD[•], followed by fast electron transfer from NAD[•] to Acr⁺-Mes to yield NAD⁺ and Acr[•]-Mes as revealed by laser flash photolysis measurements [39]. Thus, the absorption of one photon resulted in formation of two equivalents of Acr[•]-Mes (Scheme 3). Electron injection from Acr[•]-Mes to PtNPs with protons resulted in production of H₂. Cubic PtNPs with a diameter of 6.3 ± 0.6 nm exhibited the

maximum catalytic activity for the photocatalytic H_2 production [40]. The observed photocatalytic H_2 production rate was virtually same as the rate of electron injection from $\text{Acr}^\bullet\text{-Mes}$ to PtNPs [40]. The rate constant of the electron injection (k_{et}) increased linearly with increasing proton concentration [40]. When H^+ was replaced by D^+ , the inverse kinetic isotope effect was observed for the electron-transfer rate constant ($k_{\text{et}}(\text{H})/k_{\text{et}}(\text{D}) = 0.47$) [40]. The linear dependence of k_{et} on proton concentration together with the observed inverse kinetic isotope effect indicated that proton-coupled electron transfer (PCET) from $\text{Acr}^\bullet\text{-Mes}$ to PtNPs to form the Pt-H bond is the rate-determining step for the photocatalytic H_2 production (Scheme 4) [40].

Scheme 3. Mechanism of photoinduced reduction of $\text{Acr}^+\text{-Mes}$ with NADH.

Scheme 4. PCET production of H_2 with $\text{Acr}^\bullet\text{-Mes}$ on PtNPs.

When $\text{Acr}^+\text{-Mes}$ was replaced by 2-phenyl-4-(1-naphthyl)quinolinium ion ($\text{QuPh}^+\text{-NA}$), photocatalytic H_2 production with NADH and PtNPs was made possible under basic conditions (pH 10) [41]. PtNPs could be replaced by RuNPs with the virtually the same

catalytic activity for H_2 production [41]. Upon photoexcitation of QuPh^+-NA , the electron-transfer state of QuPh^+-NA ($\text{QuPh}^\bullet-\text{NA}^{*+}$) is produced, followed by electron transfer from NADH to the NA^{*+} moiety of $\text{QuPh}^\bullet-\text{NA}^{*+}$, resulting in formation of two equivalents of $\text{QuPh}^\bullet-\text{NA}$ via deprotonation of NADH^{*+} and the subsequent electron transfer from $\text{NAD}^\bullet$ to QuPh^+-NA (Scheme 5). Electron transfer from the photogenerated $\text{QuPh}^\bullet-\text{NA}$ to RuNPs resulted in H_2 evolution even under basic conditions. The rate of electron transfer from $\text{QuPh}^\bullet-\text{NA}$ to RuNPs is much faster than the rate of hydrogen evolution. RuNPs with the size of 4.1 nm exhibited the highest H_2 -evolution rate normalized by the weight of RuNPs [41]. The photocatalytic H_2 evolution with RuNPs (4.1 nm) under pH 10 conditions indicated that turnover frequency and turnover number normalized by the number of surface Ru atoms were as high as 1050 h^{-1} and 300, respectively [41]. In the case of Acr^+-Mes , electron transfer from $\text{Acr}^\bullet-\text{Mes}$ to PtNPs requires the assistance of a proton and the rate of the proton-coupled electron transfer increases with increasing proton concentration [40]. In contrast to this, electron transfer from $\text{QuPh}^\bullet-\text{NA}$ to MNPs occurs without assistance of proton because of the much stronger reducing ability of $\text{QuPh}^\bullet-\text{NA}$ as compared with

Scheme 5. Structure of QuPh^+-NA and the overall catalytic cycle for the photocatalytic hydrogen evolution with QuPh^+-NA and metal nanoparticles (MNPs, M = Ru, Pt).

$\text{Acr}^\bullet-\text{Mes}$ judging from the significantly more negative oxidation potential of $\text{QuPh}^\bullet-\text{NA}$ ($E_{\text{ox}} = -0.90 \text{ V vs SCE}$) than that of $\text{Acr}^\bullet-\text{Mes}$ ($E_{\text{ox}} = -0.57 \text{ V vs SCE}$) [37]. Thus, the

rate of electron transfer from QuPh[•]–NA to MNPs remains about the same even under highly basic conditions (pH 10). RuNPs could be replaced by NiNPs, which are more earth abundant, although the catalytic reactivity was 40% of that with commercially available PtNPs using the same catalyst weight [42].

NADH used as an electron and proton donor in Scheme 5 has been replaced by oxalic acid for the photocatalytic H₂ production with QuPh⁺–NA in a deaerated mixed solution [1:1 (v/v)] of an aqueous buffer (pH 6.0) and acetonitrile [43]. Oxalate and its conjugate acid can act as a two-electron donor to produce two equivalents of CO₂ and hydrogen (eq 1). In this case as well, the catalytic reactivity of NiNPs was 32 % of PtNPs [43].

A mixed solution of acetonitrile and water was used in the above reaction (eq 1), because of the insolubility of QuPh⁺–NA in water. In order to perform the photocatalytic production of H₂ in water, QuPh⁺–NA was incorporated into nanosized mesoporous silica-alumina with a spherical shape (sAlMCM-41) by cation exchange and the composite (QuPh⁺–NA@sAlMCM-41) was employed as a photocatalyst in water [44]. Incorporation of cationic electron donor-acceptor dyads into nanosized mesoporous silica-alumina was reported to result in much longer lifetimes of the photogenerated electron-transfer states as compared with those in solution [45,46]. The size and morphology of sAlMCM-41 were confirmed by TEM measurements and all particles were spherical and the particles sizes ranged from 200 to 700 nm [44]. In this case, K₂PtCl₆ was used as a precursor catalyst for PtNPs, because PtNPs could not be incorporated into sAlMCM-41 due to the larger size of PtNPs than the window size of sAlMCM-41 [44]. No H₂ evolution was observed under photoirradiation ($\lambda > 340$ nm) of a phthalate buffer (pH 4.5) dispersion containing QuPh⁺–NA@sAlMCM-41, sodium

oxalate and PtNPs as a photosensitizer, a sacrificial electron donor and an H₂-evolution catalyst, respectively [44]. When K₂PtCl₆ was added to the reaction solution instead of PtNPs as a precursor of H₂-evolution catalyst, however, efficient H₂ production was observed [44]. Cu(NO₃)₂ also acted as a precursor catalyst for the photocatalytic H₂ production with oxalate in water (pH 4.5) [44]. Thus, hybrid H₂-evolution catalysts derived from earth-abundant metal salts in situ provide a convenient way to develop efficient water reduction catalysts working in water as shown in Figure 2.

Figure 2. Photocatalytic production of H₂ from oxalate with QuPh⁺-N incorporated into nanosized mesoporous silica-alumina (sAlMCM-41) and Pt or Cu salts as precursor catalysts.

Under acidic conditions, oxalate anion is protonated to produce oxalic acid, which cannot act as an electron donor in the photocatalytic H₂ production system (vide supra). However, a composite photocatalytic system employing acidic oxalic acid as an electron donor has been successfully constructed by combining QuPh⁺-NA, Pt and nanosheets prepared by exfoliation of K₄Nb₆O₁₇ (niobate-NS) as an organic photosensitiser, a hydrogen-evolution catalyst and a semiconductor photocatalyst for oxidation of oxalic acid, respectively [47]. The composite photocatalyst, QuPh⁺-NA/niobate-NS (Pt), was prepared by a two-step route to locate a Pt catalyst near QuPh⁺-NA on the surfaces of

niobate-NS [47]. QuPh⁺-NA was supported on niobate-NS by a cation exchange method and then Pt was supported on the QuPh⁺-NA/niobate-NS by a photodeposition method using PtCl₄²⁻ as a precursor, which repulsively interacts with the negatively charged surfaces of niobate-NS [47]. The precursor of PtCl₄²⁻ was reduced to metallic Pt by the photocatalysis of QuPh⁺-NA in the presence of oxalic acid. Photocatalytic H₂ evolution with the composite catalyst proceeds via photoexcitation of both niobate-NS and QuPh⁺-NA to produce an electron and a hole in the semiconductor and the electron-transfer state (QuPh[•]-NA^{•+}), respectively [47].

Interconversion between H₂ and hydrogen storage compounds

Although H₂ is a promising renewable energy resource as an alternative to fossil fuels, storage and transportation of H₂ are quite difficult, because H₂ gas is explosive and its volumetric energy density is very low [48]. In the natural photosynthesis of plants, electrons and protons taken from water using solar energy are used to reduce NAD(P)⁺ to NAD(P)H, which can reductively fix CO₂ [1]. In hydrogenase-containing photosynthetic organisms such as cyanobacteria, electrons and protons taken from water using solar energy are used for the reduction of protons to hydrogen (H₂) rather than the reduction of NAD(P)⁺ to NAD(P)H [8]. Both the oxidation of H₂ with NAD(P)⁺ and the reduction of protons with NAD(P)H are catalyzed by hydrogenases [11]. There has been much effort to develop hydrogenase functional mimics, which are able to reduce protons to H₂ or to oxidize H₂ to protons [19,50-52].

Interconversion between the oxidation of H₂ with NAD(P)⁺ to produce protons and NAD(P)H and the reduction of protons with NAD(P)H to produce H₂ and NAD(P)⁺ in an aqueous solution has been made possible by using a [C,N] cyclometalated organoiridium complex ([Ir^{III}(Cp*)(4-(1H-pyrazol-1-yl-κN²)benzoic acid-κC³)(H₂O)]₂-SO₄) and by changing pH under an atmospheric pressure of H₂ at room temperature [52]. Under slightly acidic conditions (pH = 4.1), the Ir^{III}-H₂O complex (**1**) reacts with

NADH to produce the hydride complex ($[M_1-H]^0$), which reacts with H_3O^+ to produce H_2 , accompanied by regeneration of **1** (Scheme 6) [52]. The turnover frequency (TOF) was 44 h^{-1} . At pH 6.5, the carboxylic acid group of **1** is deprotonated to produce $[M_2-H_2O]$ (**2**), which reacts with H_2 to produce the hydride complex ($[M_2-H]^-$), and then the hydride complex reacts with NAD^+ to produce NADH, accompanied by regeneration of **2** (Scheme 6) with $TOF = 36\text{ h}^{-1}$ [52]. Thus the water soluble Ir complex (**1** or **2**) acts as an efficient catalyst for interconversion between H_2 and NADH

Scheme 6. Catalytic mechanism for interconversion between NADH and H_2 with a water soluble [C,N] cyclometalated Ir complexes (**1** and **2**) depending on pH.

(biological equivalent of H_2) at ambient pressure and temperature depending on pH.

Interconversion between H₂ and formic acid (HCOOH) in water at ambient temperature and pressure (eq 2) has also been made possible by using the same Ir catalyst (**1** or **2**) employed in Scheme 6 as an efficient catalyst for both directions depending on pH [53,54]. Formic acid efficiently decomposes to afford H₂ and CO₂ in the presence of **1** in acidic water (pH 2.8), whereas hydrogenation of CO₂ by H₂ occurs in the presence of **2** under an atmospheric pressure of H₂ and CO₂ in weakly basic water (pH 7.5) at room temperature [53]. Thus, HCOOH can be regarded as a liquid form of H₂ with relatively high volumetric density ($d = 1.22 \text{ g cm}^{-3}$).

The same Ir catalyst (**1**) can also act as an efficient catalyst for decomposition of paraformaldehyde to produce H₂ and CO₂ in a 2:1 mol ratio under basic conditions at room temperature [55]. At pH 11, **1** is converted to the hydroxo complex **3**, which reacts with paraformaldehyde HO(CH₂O)_nH via the monomerized and hydrated equivalent, methanediol [56], to produce the formaldehyde adduct ([Ir-OCH₂OH][−]) and HO(CH₂O)_{n-1}H [55]. The β-hydrogen elimination from [Ir-OCH₂OH][−] occurs to produce the hydride complex (**4**) and formic acid. The hydride complex (**4**) reacts with H₂O to produce H₂, accompanied by regeneration of **3** (upper-side catalytic cycle in Scheme 7) [55]. The hydroxo complex **3** also reacts with formate to produce the hydride complex (**4**) and CO₂ by β-hydrogen elimination. The hydride complex (**4**) also reacts with H₂O to produce H₂, accompanied by regeneration of **3** (lower-side catalytic cycle in Scheme 7) [55]. Thus, paraformaldehyde can be regarded as a convenient solid H₂ carrier, which has a higher energy density (6.7%) than HCOOH (4.4%).

Scheme 7. Catalytic cycles for decomposition of paraformaldehyde to H_2 and formate that is further decomposed to H_2 and CO_2 with **3**.

Conclusions

Recent advances in artificial photosynthesis for production of H_2 and storage of H_2 as liquid and solid forms have provided valuable insights on the biomimetic catalysts of combination of PSI and hydrogenases. Efficient photocatalytic production of H_2 has been made possible by using earth-abundant materials as catalysts. The catalytic

interconversion between gaseous H₂ and H₂ storage compounds (liquid or solid) has also been made possible at ambient pressure and temperature. The resulting insights are highly desired to be combined with biomimetic catalysis of PSII for water oxidation to produce H₂ from water used as electron and proton source in the near future. The challenging issue required for practical applications to produce solar fuels as an alternative to fossil fuels is the combination of efficient photocatalytic water oxidation and reduction catalysts. Recent development of robust and highly efficient molecular electrocatalysis using Ni and Co complexes [57,58] provides valuable insights into more efficient energy storage and utilization.

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Nelsen N: **Photosystems and global effects of oxygenic photosynthesis**. *Biochim Biophys Acta* 2011, **1807**:856-863.
2. Lewis NS, Nocera DG: **Powering the planet: Chemical challenges in solar energy utilization**. *Proc Natl Acad Sci USA* 2006, **103**:15729-15735.
3. Gust D, Moore TA, Moore AL: **Solar fuels via artificial photosynthesis**. *Acc Chem Res* 2009, **42**:1890-1898.
4. Wasielewski MR: **Self-assembly strategies for integrating light harvesting and**

- charge separation in artificial photosynthetic systems.** *Acc Chem Res* 2009, 42: 1910-1921.
5. Fukuzumi S, Ohkubo K: **Assemblies of artificial photosynthetic reaction centers.** *J Mater Chem* 2012, **22**:4575-4587.
 6. Fukuzumi S, Ohkubo K, Suenobu T: **Long-lived charge separation and applications in artificial photosynthesis.** *Acc Chem Res* 2014, **47**:1455-1464.
 7. Wu LZ, Chen B, Li ZJ, Tung CH: **Enhancement of the efficiency of photocatalytic reduction of protons to hydrogen via molecular assembly.** *Acc Chem Res* 2014, **47**:2177-2185.
 8. Kufryk G, **Advances in utilizing cyanobacteria for hydrogen production.** *Adv in Microbiol* 2013, **3**:60-68.
 9. King PW: **Designing interfaces of hydrogenase-nanomaterial hybrids for efficient solar conversion.** *Biochim Biophys Acta* 2013, **1827**:949-957.
 10. **Photosystem I: The light-driven plastocyanin:ferredoxin oxidoreductase.** Edited by Golbeck JH. Dordrecht: Springer; 2006.
 11. Lubitz W, Ogata, H, Rüdiger, O, Reijerse, E: **Hydrogenases.** *Chem Rev* 2014, **114**:4081-4148.
 12. Stiebritz MT, Reiher M: **Hydrogenases and oxygen.** *Chem Sci* 2012, **3**:1739-1751.
 13. • Fukuzumi S, Yamada Y, Suenobu T, Ohkubo K, Kotani H: **Catalytic mechanisms of hydrogen evolution with homogeneous and heterogeneous catalysts.** *Energy Environ Sci* 2011, **4**: 2754-2766. This perspective article summarized reaction mechanisms of hydrogen (H₂) evolution with homogeneous and heterogeneous catalysts based on kinetic studies including kinetic isotope effects.
 14. Simmons TR, Berggren G, Bacchi M, Fontecave M, Artero V: **Mimicking hydrogenases: From biomimetics to artificial enzymes.** *Coord. Chem. Rev.* 2014, **270-271**:127-150.
 15. •• Ogo S, Kabe R, Uehara K, Kure B, Nishimura T, Menon SC, Harada R, Fukuzumi S, Higuchi Y, Ohhara T, Tamada T, Kuroki R: **A dinuclear Ni(μ -H)Ru complex derived from H₂.** *Science* 2007, **316**:585-587 A paramagnetic dinuclear nickel-ruthenium complex with a bridging hydrido ligand from the heterolytic cleavage of H₂ by a dinuclear NiRu aqua complex in water under ambient conditions. The structure of the hexacoordinate Ni(μ -H)Ru complex was unequivocally determined by neutron diffraction analysis. The results suggest that

the RuNiH core could be described as $\text{Re-H}^-\bullet\bullet\text{Ni}$, which indicates that the Ni(II) serves as a Lewis acid to stabilize the hydride. Such insights would otherwise be unattainable by studies on the enzyme itself, because protein crystallography cannot detect hydride ligands.

16. • Ogo S, Ichikawa K, Kishima T, Matsumoto T, Nakai H, Kusaka K, Ohhara T: **A Functional [NiFe]hydrogenase mimic that catalyzes electron and hydride transfer from H_2** . *Science* 2013, **339**:682-684 This paper report the first structural and functional [NiFe]-based model of [NiFe]hydrogenase enzymes. The neutron-scattering analysis revealed that the hydride ion was located on the Fe center. This complex heterolytically activates hydrogen to form a hydride complex that is capable of reducing substrates by either hydride ion or electron transfer.
17. • Fukuzumi S, Yamada Y: **Catalytic activity of metal-based nanoparticles for photocatalytic water oxidation and reduction**. *J Mater Chem* 2012, **22**:24284-24296. This feature article focuses on the catalytic activity of non-Pt metal nanoparticles for the photocatalytic H_2 production from water as well as water oxidation.
18. • Fukuzumi S, Hong D, Yamada Y: **Bioinspired photocatalytic water reduction and oxidation with earth-abundant metal catalysts**. *J Phys Chem Lett* 2013, **4**:3458-3467. This perspective article summarized the development of earth-abundant metal catalysts for photocatalytic water reduction and oxidation, inspired by structure and functions of hydrogenases and oxygen evolving center in PSII.
19. • Fukuzumi S, Suenobu T: **Hydrogen storage and evolution catalysed by metal hydride complexes**. *Dalton Trans* 2013, **42**:18-28. This perspective article summarized the current status of H_2 storage and evolution using various hydrogen donors (formic acid, NADH and alcohols), which are catalyzed by metal hydride complexes. The catalytic mechanisms of the H_2 storage and evolution are discussed by focusing on the reactivity of metal-hydride complexes.
20. Lubner CE, Grimme R, Bryant DA, Golbeck JH: **Wiring photosystem I for direct solar hydrogen production**. *Biochemistry* 2010, **49**:404-414.
21. SBtif, P: **Ferredoxin and flavodoxin reduction by photosystem 1**. *Biochim Biophys Acta* 2001, **1507**:161-179.
22. • Ihara M, Nishihara H, Yoon KS, Lenz O, Friedrich B, Nakamoto H, Kojima K, Honma D, Kamachi T, Okura I: **Light-driven hydrogen production by a hybrid**

- complex of a [NiFe]-hydrogenase and the cyanobacterial photosystem I.** *Photochem Photobiol* 2006, **82**: 676-682 This paper reports the first example of a light-driven H₂ production by an artificial complex between a [NiFe]-hydrogenase and the cyanobacterial PSI, representing an important step on the way to design a photosynthetic organism that efficiently converts solar energy and water into H₂.
23. Ihara M, Nakamoto H, Kamachi T, Okura I, Maeda M: **Photoinduced hydrogen production by direct electron transfer from photosystem I cross-linked with cytochrome *c*₃ to [NiFe]-hydrogenase.** *Photochem Photobiol* 2006, **82**:1677-1685.
 24. Greenbaum E: **Platinized chloroplasts: A novel photocatalytic material.** *Science* 1985, **230**:1373-1375.
 25. Utschig LM, Dimitrijevic NM, Poluektov OG, Chemerisov SD, Mulfort KL, Tiede DM: **Photocatalytic hydrogen production from noncovalent biohybrid photosystem I/Pt nanoparticle complexes.** *J Phys Chem Lett* 2011, **2**:236-241.
 26. Grimme RA, Lubner CE, Golbeck JH: **Maximizing H₂ production in photosystem I/dithiol molecular wire/platinum nanoparticle bioconjugates.** *Dalton Trans* 2009, 10106-10113.
 27. Gorka M, Schartner J, van der Est A, Rögner M, Golbeck JH: **Light-mediated hydrogen generation in photosystem I: Attachment of a naphthoquinone-molecular wire-Pt nanoparticle to the A_{1A} and A_{1B} sites.** *Biochemistry* 2014, **53**:2295-2306.
 28. Brown KA, Wilker MB, Boehm M, Dukovic G, King PW: **Characterization of photochemical processes for H₂ production by CdS nanorod-[FeFe] hydrogenase complexes.** *J Am Chem Soc* 2012, **134**:5627-5636.
 29. Wilker MB, Shinopoulos KE, Brown KA, Mulder DW, King PW, Dukovic G: **Electron transfer kinetics in CdS nanorod-[FeFe]-hydrogenase complexes and implications for photochemical H₂ generation.** *J Am Chem Soc* 2014, **136**:4316-4324.
 30. Brown GM, Brunschwig BS, Creutz C, Endicott JF, Sutin N: **Homogeneous catalysis of the photoreduction of water by visible light. Mediation by a tris(2,2'-bipyridine)ruthenium(II)-cobalt(II) macrocycle system.** *J Am Chem Soc* 1979, **101**:1298-1300.
 31. Grätzel M: **Artificial photosynthesis: water cleavage into hydrogen and oxygen**

- by visible light. *Acc Chem Res* 1981, **14**:376-384.
32. Darwent JR, Douglas P, Harriman A, Porter G, Richoux MC: **Metal phthalocyanines and porphyrins as photosensitizers for reduction of water to hydrogen.** *Coord Chem Rev* 1982, **44**:83-126.
 33. Deponti E, Luisa A, Natali M, Iengo E, Scandola F: **Photoinduced hydrogen evolution by a pentapyridine cobalt complex: elucidating some mechanistic aspects.** *Dalton Trans* 2014, in press DOI: 10.1039/c4dt02269f
 34. Lv H, Guo W, Wu K, Chen Z, Bacsá J, Musaev DG, Geletii YV, Lauinger SM, Lian T, Hill CL: **A noble-metal-free, tetra-nickel polyoxotungstate catalyst for efficient photocatalytic hydrogen evolution.** *J Am Chem Soc* 2014, **136**:14015-14018.
 35. • Fukuzumi S, Kobayashi T, Suenobu T: **Photocatalytic production of hydrogen by disproportionation of one-electron-reduced rhodium and iridium-ruthenium complexes in water.** *Angew Chem Int Ed* 2011, **50**:728-731 This paper clarified how photoinduced electron transfer of a photosensitizer (a one-electron process) leads to H₂ production (a two-electron process) via disproportionation of the one-electron-reduced metal complexes.
 36. • Fukuzumi S, Kotani H, Ohkubo K, Ogo S, Tkachenko NV, Lemmetyinen H: **Electron-transfer state of 9-mesityl-10-methylacridinium ion with a much longer lifetime and higher energy than that of natural photosynthetic reaction center.** *J Am Chem Soc* 2004, **126**:1600-1601 This paper reports the first example of a simple electron donor-acceptor dyad (9-mesityl-10-methylacridinium ion) affording the photogenerated electron-transfer state, which has a much longer lifetime and higher energy than that of the photosynthetic reaction center, by minimizing the reorganization energy of electron transfer without loss of energy due to multistep electron-transfer processes.
 37. Kotani H, Ohkubo K, Fukuzumi S: **Formation of a long-lived electron-transfer state of a naphthalene-quinolinium ion dyad and the π -dimer radical cation.** *Faraday Discuss* 2012, **155**:89-102.
 38. Kotani H, Ohkubo K, Takai Y, Fukuzumi S: **Viologen-modified platinum clusters acting as an efficient catalyst in photocatalytic hydrogen evolution.** *J Phys Chem B* 2006, **110**:24047-24053.
 39. Kotani H, Ono T, Ohkubo K, Fukuzumi S: **Efficient photocatalytic hydrogen evolution without an electron mediator using a simple electron donor-acceptor**

- dyad. *Phys Chem Chem Phys* 2007, **9**:1487-1492.
40. Kotani H, Hanazaki R, Ohkubo K, Yamada Y, Fukuzumi S: **Size- and shape-dependent activity of metal nanoparticles as hydrogen-evolution catalysts: Mechanistic insights into the electron-transfer injection step.** *Chem Eur J* 2011, **17**:2777-2785.
 41. • Yamada Y, Miyahigashi T, Kotani H, Ohkubo K, Fukuzumi S: **Photocatalytic hydrogen evolution under highly basic conditions by using Ru nanoparticles and 2-phenyl-4-(1-naphthyl)quinolinium ion.** *J Am Chem Soc* 2011, **133**:16136-16145. Photocatalytic hydrogen evolution with a ruthenium metal catalyst under basic conditions (pH 10) has been made possible for the first time by using 2-phenyl-4-(1-naphthyl)-quinolinium ion (QuPh⁺-NA), NADH, and Ru nanoparticles (RuNPs) as the photocatalyst, electron donor, and hydrogen-evolution catalyst, respectively. RuNPs have been demonstrated to exhibit comparable catalytic activity to PtNPs.
 42. Yamada Y, Miyahigashi T, Kotani H, Ohkubo K, Fukuzumi S: **Photocatalytic hydrogen evolution with Ni nanoparticles by using 2-phenyl-4-(1-naphthyl)quinolinium ion as a photocatalyst.** *Energy Environ Sci* 2012, **5**:6111-6118.
 43. Yamada Y, Miyahigashi M, Ohkubo K, Fukuzumi S: **Photocatalytic production of hydrogen with 2-phenyl-4-(1-naphthyl)-quinolinium ion and oxalate.** *Phys Chem Chem Phys* 2012, **14**:10564-10571.
 44. Yamada Y, Tadokoro H, Fukuzumi S: **Hybrid H₂-evolution catalysts: in situ formation of H₂-evolution catalysts from metal salts inside mesopore of silica-alumina supporting an organic photosensitiser.** *RSC Adv* 2013, **3**:25677-25680.
 45. Fukuzumi S, Doi K, Itoh A, Suenobu T, Ohkubo K, Yamada Y, Karlin KD: **Formation of a long-lived electron-transfer state in nanosized mesoporous silica-alumina enhances photocatalytic oxidation reactivity with a copper complex.** *Proc Natl Acad Sci USA* 2012, **109**:15572-15577.
 46. Yamada Y, Nomura A, Ohkubo K, Suenobu T, Fukuzumi S: **Long-lived electron transfer state of 2-phenyl-4-(1-naphthyl)quinolinium ion incorporated into**

- nanosized mesoporous silica-alumina acting as a robust photocatalyst in water.** *Chem Commun* 2013, **49**:5132-5134.
47. Yamada Y, Nomura A, Tadokoro H, Fukuzumi S: **A composite photocatalyst of an organic electron donor-acceptor dyad and a Pt catalyst supported on semiconductor nanosheets for efficient hydrogen evolution from oxalic acid.** *Catal Sci Technol* 2014, in press.
 48. • Fukuzumi S: **Bioinspired energy conversion systems for hydrogen production and storage.** *Eur J Inorg Chem* 2008:1351-1362 This is a review on developments in photocatalytic hydrogen production by using artificial photosynthesis systems together with those in hydrogen storage through the fixation of CO₂ with H₂.
 49. Magnuson, A.; Anderlund, M.; Johansson, O.; Lindblad, P.; Lomoth, R.; Polivka, T.; Ott, S.; Stensjö, K.; Styring, S.; Sundström, V.; Hammarström, L: **Biomimetic and microbial approaches to solar fuel generation.** *Acc. Chem. Res.* 2009, **42**:1899-1909.
 50. Kaur-Ghumana, Sandeep; Stein, M: **[NiFe] hydrogenases: How close do structural and functional mimics approach the active site?** *Dalton Trans.* **2014**, **43**:9392-9405.
 51. Simmons, Trevor R.; Artero, V: **Catalytic hydrogen oxidation: Dawn of a new iron age.** *Angew. Chem., Int. Ed.* 2013, **52**:6143-6145.
 52. • Maenaka Y, Suenobu T, Fukuzumi S: **Efficient catalytic interconversion between NADH and NAD⁺ accompanied by generation and consumption of hydrogen with a water-soluble iridium complex at ambient pressure and temperature.** *J Am Chem Soc* 2011, **134**:367-374 This is the first report on catalytic interconversion between NADH and H₂ at ambient pressure and temperature by using a [C,N] cyclometalated organoiridium complex. The corresponding iridium hydride complex formed under an atmospheric pressure of H₂ undergoes the 1,4-selective hydrogenation of NAD⁺ to form 1,4-NADH, whereas in weakly acidic water the hydride complex formed by the reduction of the Ir(III) complex with NADH reacts with proton to produce H₂.
 53. Maenaka Y, Suenobu T, Fukuzumi S: **Catalytic interconversion between hydrogen and formic acid at ambient temperature and pressure.** *Energy Environ Sci* 2012, **5**:7360-7367.
 54. • Hull JF, Himeda Y, Wang WH, Hashiguchi B, Periana R, Szalda DJ, Muckerman

- JT, Fujita E: **Reversible hydrogen storage using CO₂ and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures.** *Nat Chem* 2012, **4**: 383-388 This paper also reports that a dinuclear Ir(Cp*) complex with 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine (thbpym) as a bridging ligand, [$\{\text{Ir}(\text{Cp}^*)(\text{Cl})\}_2(\text{thbpym})\]^{2+}$, acts as a pH-modulated catalyst for interconversion between H₂ and HCOOH by the deprotonation equilibrium of the phenolic ligand.
55. Suenobu T, Shibata S, Fukuzumi S: **Catalytic hydrogen production from paraformaldehyde and water with an organoiridium complex.** *Chem Commun* 2014, in press.
 56. Nielsen M, Alberico E, Baumann W, Drexler HJ, Junge H, Gladiali S, Beller M: **Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide.** *Nature* 2013, **495**: 85-89.
 57. DuBois DL: **Development of molecular electrocatalysts for energy storage.** *Inorg. Chem.* 2014, **53**: 3935-3960.
 58. Bullock RM, Appel AM, Helm ML: **Production of hydrogen by electrocatalysis: making the H-H bond by combining protons and hydrides.** *Chem. Commun.* 2014, **50**: 3125-3143.