Artificial Photosynthesis: Learning from Nature
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Artificial photosynthesis has been devised and investigated in pursuit of solving the 21st century's energy problem. Despite significant advances in recent decades, applying the technology in real life is still a challenging subject for scientists. As the term “artificial photosynthesis” stems from mimicking natural photosynthesis, we can learn from nature’s strategies which have evolved over 3.4 billion years. This Review highlights important strategies of natural photosynthesis which can be borrowed for highly efficient and robust artificial photosystems for solar fuel production. Starting with a brief description of photosystem II in natural photosynthetic autotrophs, three relevant bioinspired strategies are discussed in this article: i) accumulative charge transfer, ii) photoprotection, and iii) self-healing. Next, development of artificial photosystems mimicking those strategies will be discussed. Finally, remaining challenges and perspectives for future development of artificial photosynthesis are described.

1. Introduction

Photosynthetic autotrophs have been converting photon energy to chemical energy for 3.4 billion years; some of the converted energy was deposited on earth as forms of fossil fuels. Currently, human beings are consuming 13 TW of energy, in which 81% is based on combustion of fossil fuels. Along with the fast depletion of fossil fuels, the use of carbon-based fuels inevitably produces air pollution and greenhouse gases. To solve this conflict between energy demand and ecological issues, sustainable and clean technologies for energy production are required. Sun provides 171 000 TW energy on the surface of the earth, thus utilizing only 0.01% of it will be just enough to meet the whole need of energy by human beings. In this context, developing a system which can convert the photon energy to chemical energy is of great importance for the solar flux utilization.

Natural photosynthesis utilizes solar energy to convert water and/or carbon dioxide into higher energy components such as carbohydrates. Artificial photosynthesis replicates the photochemical process of natural photosynthesis, however, it is more dedicated to the production of useful fuels or valuable chemicals such as molecular hydrogen (H₂), methane, methanol, etc. The first idea of artificial photosynthesis dates back to the beginning of 1900s when Giacom Ciancian commented in his paper that human should shift from consuming fossil fuels to generating sustainable energy from the sun. The first experimental demonstration of light-driven water splitting was so called “Honda–Fujishima effect”. The photoelectrochemical cell (PEC) was composed of TiO₂ photoanode and platinum black cathode. By illumination of the photoanode (λ > 400 nm), O₂ and H₂ were generated at the photoanode and cathode, respectively. The same group reported a photocatalytic CO₂ reduction with aqueous suspension of various semiconductor particles. Since the pioneering works by Honda and Fujishima, enormous efforts have been made in pursuit of efficient, stable and cost-effective artificial photosystems for water splitting and CO₂ reduction.

Nature has developed several strategies to run the photochemical processes of photosynthesis in an efficient and robust way: i) accumulative charge transfer to run the multi-electron process of product production efficiently, ii) photoprotection to prevent the system from being damaged by excess photon flux, and iii) self-healing to repair or replace damaged proteins prolong the activity of whole system. Those strategies have been developed to balance the maximum efficiency and sustainability upon fluctuating environmental conditions. Thus, closely mimicking these nature’s strategies is a challenging but promising approach to realize the efficient and stable artificial photosynthesis in real life application. This approach has received recent attention, and many research groups are currently developing molecular components which mimic the natural photosystem for solar fuel production.

In this contribution, we would illustrate recent progresses on molecular systems for artificial photosynthesis by mimicking the nature’s strategies. There is another research area of biohybrid systems directly using the part of nature, i.e., bacteria or enzymes, which will not be discussed in this paper.

2. Overview of Photosystem II (PSII)

Production of organic matter and maintenance of most forms of life on Earth is maintained by oxygenic photosynthesis process. This process converts light energy from sun into chemical energy, which is stored as highly reduced organic compounds. Two main photosynthetic reaction centers (RC) namely, photosystem I (PSI) and PSII, are responsible for linear electron transport in oxygenic photosynthesis. In early 20th century Emerson and Arnold reported that hundreds of chlorophyll (Chl) molecules operated together to produce one oxygen molecule. This network of Chl molecules, which supplied excitation energy to photochemical catalytic center, was later on named as “photosynthetic unit”. In 1960 Hill and Bendall proposed that a two-pigment system worked in series in order to realize oxygenic photosynthesis where short-wavelength reaction and a long wavelength reaction take place. This hypothesis of Hill and Bendall, called zigzag model or “Z-Scheme” was experimentally proved by several studies in 1961 and the terms PSI and PSII were coined. PSII, which is a multi-subunit membrane protein that has the unique ability to extract electrons from water to result in molecular oxygen (O₂) upon reduction of
plastoquinone. PSII constitutes at least 25 different protein subunits many of which are bound to the thylakoid membrane. However, minimal reaction center responsible for charge and is then reduced once more and reduction process or CO reduction are multi-electron processes. The process starts with capturing of light energy by pigments within the antenna system. Then the energy is transferred to the Chlorophylls (Chls) that involves the primary electron donor, P680, to generate an excited singlet state, P680*. Excited state relaxes back by reducing a nearby Pheophytin (Pheo), a molecule similar to Chl in structure but missing the central Mg ion, forming the primary radical pair P680’-Pheo’. Reduced Pheophytin, Pheo’, then oxidized back to Pheo by giving an electron to the primary plastoquinone electron acceptor, Qa, attached to the D2 protein. The electron is then transferred to the secondary plastoquinone electron acceptor, Qb, bound to D1. Qb is then reduced once more and gets protonated to yield the plastoquinol, QbH2. After leaving the PSII system, this molecule is replaced by an oxidized plastoquinone molecule from a pool of plastoquinone molecules located in the lipid bilayer. P680+, the oxidized primary donor, is reduced by a redox-active tyrosine residue, Tyr 161 of the D1 protein. Tyr 161 is afterwards reduced by the MnCa cluster, coordinated by aspartate, glutamate, and histidine residues in the D1 protein, including the C-terminus of mature D1, and by residual glutamate of CP43. The MnCa cluster exists in five distinct oxidation or S states termed S0-S4, where the subscript indicates the number of accumulated oxidizing equivalents. One molecule of oxygen occurs from two moles of water after formation of the S1 state, resetting the enzyme to the S2 state, and so occurs with a periodicity of four.

### 3. Accumulative Charge Transfer

Water splitting and CO2 reduction are multi-electron processes (Scheme 1), which implies that multiple electrons should be accumulated at the catalytic center to run the photochemical cycles. Even for the simplest processes for H2 production or CO formation, it requires two electrons accumulated to a catalyst. It should be noted that in general, photon absorption is a monoelectronic process, results in single charge separation. In this context, it is required to accumulate multiple electrons or holes with several rounds of successive single photon absorption before charge recombination occurs.

In PSII apparatus, multiple rounds of single electronic absorption are successfully coupled with extraction of four electrons from the MnCa cluster to run water oxidation. The mechanism of water oxidation by PSII has been extensively investigated so far. Schematic representation of the key cofactors in PSII is shown in Figure 1a. The photolytic cycle starts with light absorption of the chlorophyll pigment (P680) to form a photoexcited state (P680*), followed by charge separa-

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**Figure 1.** a) Arrangement of cofactors in PSII; b) S-states for the formation of O2 proposed by Kok and co-workers. Reproduced with permission from Ref. [55]. Copyright (2007) Elsevier B. V.

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tion to generate radical cation (P680\(^{+}\)). The hole can further be transferred to multi-electron-donor of tetramanganese cluster (CaMn\(_4\)) through tyrosine (Y\(_{2}\)) as a charge transfer mediator. It had been generally accepted that sequential extraction of four electrons from CaMn\(_4\) is responsible for the catalytic cycle for water oxidation (Figure 1b).

Five-step reaction of CaMn\(_4\), denoted as S\(_2\) through S\(_4\), can be realized upon consecutive charge transfer, where S\(_2\) is the ground state and S\(_4\) is the four electron oxidized state. The S\(_4\) state of CaMn\(_4\) is quite unstable and rapidly reacts with water to produce O\(_2\).

3.1. Accumulation of Electrons

Wasielewski and co-workers first reported an accumulation of two electrons in a donor-acceptor-donor triad where two free-base porphyrin donors are attached to a two-electron acceptor of \(N,N'\)-diphenyl-3,4,9,10-perylenebis(dicarboximide) (PBDCI) unit (Figure 2a).

Upon flash photolysis of the porphyrin units with high laser intensities (up to 20 photons/molecule), the PBDCI unit was doubly reduced to give PBDCI\(^{2-}\) and two holes were stored in each porphyrin units; only single charge separation was observed with low laser intensities (<50 photons/molecule). Imahori and co-workers reported a similar system where tetracyanoanthraquinodimethane (TCAQ) and zinc porphyrin were employed as acceptor and units, respectively (Figure 2b).

Formation of doubly reduced TCAQ was successfully demonstrated using double pulse technique: i) first pulse of 532 nm laser was used to photogenerate the single charge separated state and ii) second pulse was delayed by 233 ps and set to 555 nm to selectively photoexcite the unexcited porphyrin units. Due to the distinct optical properties of singly- and doubly-reduced acceptor units, possible application of this molecular system as an optical switch was proposed instead of artificial photosynthesis. However, pioneered by these works, several examples of accumulative electron transfer in molecular systems aiming on the multiple electrons utilization in artificial photosynthesis.

A first principle for the accumulative electron transfer in APS is to store multiple electrons in one molecule to run the catalytic cycles. Molecular electron-reservoirs are compounds, which can store and transfer multi-electrons stoichiometrically or catalytically without decomposition or side reaction. However, the electron reservoir property in organometallic compounds is restricted to some classes of compounds that can withstand multiple redox changes without molecular disruption. Especially for the transition metal complexes, it has been noted that the population of d orbital upon photoexcitation or multiple reduction is a main reason of the degradation of organometallic complexes. Electron reservoirs can be designed with following strategies: i) the population of d orbital can be prevented if the orbitals affected by the electron addition are delocalized over an extended ligand framework, and ii) tethering multiple electron acceptors which can store and stabilize excessive electrons in each electron reserving units.

The Park group recently reported a Pt\(^{4+}\) water reduction catalyst (WRC) using the electron reservoir strategies. Specially designed tetraphenylsilane (TPS) substituent was introduced to a dinine ligand of a molecular Pt\(^{4+}\) WRC (TPSPtCl\(_2\) in Figure 3).

TPS has a tetrahedral configuration where four phenyl rings are attached to a central Si atom. The extended \(\pi\)-systems enable delocalization of excess electrons over the ligands, thus improve electron-reservoir character of the Pt\(^{4+}\) WRC. Electrochemical study and density functional theory (DFT) based quantum chemical approach revealed that TPS groups in TPSPtCl\(_2\) create electron-reservoir characteristics and dramatically enhanced electrochemical stability upon two-electron reduction. A turnover number of 510000 was recorded for photocatalytic water reduction, which represents a large improvement over the control complexes that do not contain the TPS substituents.

Sakai and co-workers reported a series of Pt\(^{4+}\) WRCs which contains pyridinium or methyl viologen moieties as electron storing moieties. A simple Pt\(^{4+}\) terpyridyl complex with a methyl pyridinium periphery, namely PV\(^{2+}\), was synthesized and tested for light-driven H\(_2\) production in combination with ethylenediaminetetraacetic acid (EDTA, YH\(_4\)) as a sacrificial electron donor (Figure 4a). It was found that PV\(^{2+}\) formed a doubly-reduced species PV\(^{2+}\) by two consecutive photoinduced electron transfer (PET) steps, namely: [PV\(^{4+}\)···YH\(_4\)\(^{2+}\) \(\rightarrow\) PV\(^{2+}\)···YH\(_2\)\(^{2+}\) \(\rightarrow\) PV\(^{0}\) \(\rightarrow\) YH\(_4\)]. This molecular system well mimics the Z-Scheme, although the two reductive quenching
processes do not perfectly match with the oxidative ones in natural photosynthesis (Figure 4b). As a result, PV$_2^{2+}$ recorded a TON of 4.1 after 12 h of photoirradiation, which is ca. 10 times larger than that of [Pt(tpy)Cl]$^+$ (TON = 0.4).

Another class of Pt$^{II}$ poly(pyridine) derivatives with viologen units was reported by the same research group (Figure 5a). The catalytic activity of the complex was enhanced by tethering viologen units as electron acceptors, which can temporarily collect the high-energy electrons generated during the photoinduced steps. In the case of the viologen-containing complexes, the ground state of the photosensitizing site, i.e., PtCl$_2$(bpy) was immediately regenerated from its reduced form after the first PET step, thus restoring the light absorption ability (Figure 5b). As a result, the Pt$^{II}$ bipyridyl complex with four viologen periphery, [PtCl$_2$(5,5'-MV4)]$^{8+}$, recorded one order of magnitude higher TON of 27 after 12 h of photolysis compared to PV$_2^{2+}$.[74] Further series study was carried out and TONs of 35 and 25.2 were recorded with a Pt$^{II}$ bipyridyl complex[79] and a Pt$^{II}$ terpyridyl complex[76] respectively. With the same strategy, Ru$^{II}$-based photosensitizers with peripheral methyl viologen units were designed to store and transfer multiple electrons to colloidal Pt WRC. Storing up to 8 electrons in a single photosensitizer was achieved by tethering 12 methyl viologen units to a [Ru$^{III}$(bppy)]$_{2}^{2+}$ center.[77,76]

The Brewer group reported a series of trinuclear complexes with a molecular structure of [(TL$_2$Ru$^{II}$BL)$_2$M$_{III}$X$_2$]$^{5+}$ (TL = terminal ligand, BL = bridging ligand, M = Ir or Rh, and X = halogen ligand).[79–81] Two photosensitizing Ru$^{II}$ units were bridged to the central electron accepting units to direct the accumulation of electrons. While Ir$^{III}$ center can store two electrons in its ligands without affecting the oxidation state of the metal center, Rh$^{II}$-based complexes undergo metal-centered reduction to form Rh$^{I}$ species upon one electron reduction. Then Rh$^{I}$ intermediate disproportionates to form Rh$^{II}$ and Rh$^{III}$ species with loss of the two chloride ligands. The free coordination site of Rh$^{I}$ then opens a possibility for substrates such as proton to anchor to form metal-hydride, followed by H$_2$ production. Several Rh$^{III}$-based trinuclear complexes were subjected to photocatalytic H$_2$ production[82–85] and TON of 1300 was recorded with [((Ph$_2$phen)$_2$Ru(dp))$_2$RhBr$_2$]$^{9+}$ (Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline and dp = 2,3-bis(2-pyridyl)pyrazine, Figure 6a) in combination with N,N'-dimethylaniline (DMA) as a sacrificial electron donor.[85] Recently, Collomb and co-workers developed a trinuclear complex Ru$_2$Rh, where two Ru$^{II}$ photosensitizing units are linked to the Rh$^{III}$ center with a bridging ligand of 1,2-bis(4'-methyl-2,2'-bipyridinyl)ethane (Figure 6b).[86] Non-conjugated ligand was used to minimize the electronic coupling between the photosensitizing and electron accepting units thus maintain the original physical proper-

![Figure 4. Chemical structure of a) Pt WRCs and b) Z-Scheme of PV$^{2+}$. Reproduced with permission from Ref.[76]. Copyright (2016) The Royal Society of Chemistry.](image)

![Figure 5. Chemical structures of a) Pt-MVs and b) charge transfer scheme. Reproduced with permission from Ref. [76]. Copyright (2016) The Royal Society of Chemistry.](image)

![Figure 6. Chemical structures of a) non-bridged and b) bridged Ru$_2^{II}$-Rh$^{III}$–Ru$_2^{II}$ supramolecular complexes.](image)
ties of parent molecules, i.e., \([\text{Ru}^{II}(\text{bpy})_3]^2^+\) and \([\text{Rh}^{III}(\text{bpy})_2\text{Cl}_2]^+\). The authors highlighted a high TON of 430 in pure aqueous system, however, it has been noted that the photocatalytic activities of the polynuclear systems have been rather low compared to those of multi-component systems.\(^{[87]}\)

### 3.2. Accumulation of Holes

Tetramanganese cluster is responsible for the accumulation of four holes for \(\text{O}_2\) evolution from water in PSII, vide supra. With this in mind, several photosensitizer/donor or photosensitizer-donor systems have been made to mimic the charge accumulation, where the donors are based on mono- or polynuclear manganese complexes. Styring and co-workers reported either inter- and intra-molecular accumulation of holes in dinuclear Mn\(_{2}^{II,II}\) unit in combination with Ru\(^{II}\) polypyridine moiety as a photosensitizer (Figure 7a).\(^{[88–90]}\) In the presence of pentaaminechlorocobalt\(^{III}\) chloride as an electron acceptor, photoexcitation of Ru\(^{II}\) center resulted in a stepwise extraction of two electrons from the Mn\(_{2}^{II}\) unit. EPR spectroscopy revealed continuous formation of Co\(^{II}\) species and Mn\(_{2}^{II,IV}\) species, indicating that three holes were accumulated in the dinuclear manganese moiety (Figure 7b).\(^{[90]}\) Collomb and Deronzier et al. reported similar systems where three Ru\(^{II}\) tris(bipyridine) complexes are tethered to a Mn\(^{II}\) tris(bipyridine) center.\(^{[91, 92]}\) It was proposed in these studies that upon one electron reduction of the Mn\(^{II}\) center, the manganese complex were decomposed and irreversibly transformed into corresponding di-\(\mu\)-oxo bridged Mn\(_{2}^{III,IV}\) dimeric species (Figure 7c). Despite the presence of Mn\(^{II}\)-based units, those systems did not show any catalytic activity of \(\text{O}_2\) production from water.

Recently, dye-sensitized inorganic/organic hybrid systems have been proposed to be an alternative approach for facilitating accumulative charge transfer in molecular systems. Inorganic nanocrystals such as TiO\(_2\) nanocrystals can utilized as an electron/hole reservoir. Therefore, hybridizing them with organic/organometallic dyes offers multiple charge separation after several rounds of single photon excitation. The Hammerström group reported a series of inorganic/organometallic hybrid systems where Ru\(^{II}\)polypyridine photosensitizers with oligotriarylamine (OTA) donors are linked to TiO\(_2\) nanoparticles as an acceptor.\(^{[93, 94]}\) Careful and intensive study in combination with double pulse experiments showed efficient accumulative electron transfer resulting in the formation of two-electron oxidized state of the OTA unit upon successive excitation by two photons. Among the systems studied, one with OTA-Ru dye anchored onto nanocrystalline TiO\(_2\) (Figure 8) showed efficient accumulative electron transfer upon successive photoexcitation with double pulse experiments. Once the Ru\(^{II}\) photosensitizer was photoexcited by first excitation pulse, the exciton was in-

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**Figure 8.** Chemical structure of OTA-Ru. Reproduced with permission from Ref. [93]. Copyright (2010) American Chemical Society.

**Figure 7.** a) Schematic of chemical reaction sensitized by Ru\(^{II}(\text{bpy})_3\)). b) Decrease of Mn\(_{2}^{III}\) and increase of Mn\(_{2}^{III,IV}\) signal amplitude as a function of number of flashes. c) Process of formation of di-\(\mu\)-oxo dimeric species. Reproduced with permission from Refs. [88] and [92]. Copyright (2002) Elsevier for Figure 7a and 7b; copyright (2006) The Royal Society of Chemistry for Figure 7c.
jected rapidly into the TiO$_2$ nanocrystal within 1 ps to form Ru$^{III}$ species. Then the ground state of Ru$^I$ center was recovered by oxidizing OTA within 1 ns regime, resulting in TiO$_2$(Ru$^{III}$-OTA)$^+$ state. With second photoexcitation, one more round of charge separation occurred to yield doubly charge separated state of TiO$_2$(Ru$^{III}$-OTA)$_2^+$. The overall yield of accumulative charge transfer was reported as high as 100%.

4. Photoprotection

The intensity of the solar radiation fluctuates and whenever the light intensity is greater than that needed to saturate the photosynthesis, the plant or algae faces a danger of being damaged by the excess of incoming photons. For example, when light absorption exceeds the capacity of photosystem in PSII, triplet excited state of chlorophyll (3Chl) is generated either by intersystem crossing from its singlet excited state (1Chl) or by charge recombination of the primary radical pairs between PSII primary donor and pheophytin (P680$^+$/Phe$^-$). The 3Chl is a potent sensitizer for molecular oxygen forming singlet oxygen (1O$_2$) which can cause oxidative damage to the pigments, lipids and proteins of the photosynthetic system. To cope with fluctuating irradiance and prevent the cell or protein from getting damaged, photosynthetic organisms have evolved several photoprotective mechanisms: i) adjustment of light-harvesting antenna size, ii) thermal dissipation of excess absorbed light energy, and iii) scavenging reactive oxygen species.$^{[95–110]}$ The regulation of excess photons thus can prolong the lifetime of the photosynthetic apparatus. Achieving self-regulating behavior in molecular system is a critical challenge to prolong the artificial photosynthesis.

4.1. Adjustment of Light-Harvesting Antenna Size

One implication is that the light-harvesting antennas in Chls can rearrange in their protein matrix upon either a long term or a short term fluctuation of light intensity.$^{[111,112]}$ During long-term acclimation to fluctuating light intensities, changes in antenna size are due to changes in light-harvesting chlorophyll protein complex (LHCs gene expression$^{[113–115]}$) and/or LHCs degradation.$^{[116]}$ In short term modulation of the antenna sizes, overexcitation of PSII results in detachment of LHCs from PSII, thus decreases the effective size of LHCs.$^{[117]}$ In both cases, the overall light absorption of photosystem can be reversibly modulated with different light intensity.

Molecular logic gate strategy can be borrowed to realize the light-intensity dependent regulation of photochemical processes. A molecular logic gate is a molecule that performs a logical operation based on physical or chemical inputs. Once the logic gate is operated by means of photons, that is, photochromic molecule, we can modulate the photophysical properties of the molecule thus give ways to form a photon regulator. Either photoinduced intramolecular energy or electron transfer processes have been successfully controlled by using the photochromic units. Effenberger and co-workers developed a D-B-A system with ON/OFF photoswitchable intramolecular energy transfer by incorporation of a photochromic fulgimide between anthracene and coumarin (Figure 9a).$^{[118]}$ Tsuchiya reported an optical control of photo-induced electron transfer by incorporating two porphyrin units with a photosomerizable azobenzene linker (Figure 9b).$^{[119]}$ Inspired by those works, significant efforts have been made on the development of artificial photoregulation systems on catalysts for chemical reactions, however, most of the works have been focusing on the light-induced activation of the catalytic processes and downregulation of the catalytic activities are still scarce.$^{[120]}$ Although actual photoregulation has not been shown in those papers, they provided a good photophysical background for using those systems for photoregulation in artificial photosynthesis.

The molecular logic gate concept was successfully adapted to molecular photoregulatory system. Gust and co-workers reported a series of supramolecular systems which can downregulate the high intensity light by activation of by using thermally-reversible photochromic units which can reverse the photochemical process by thermal energy (Figure 10)$^{[121]}$. In the ground state, the dye exists in the dihydroindololazine (DHI) form (1c) which can absorb only blue lights. When 1c absorbs light, it photosomerizes into an open form of colored betaine (BT), depicted as 1o. Molecule 1o thermally converts back to 1c with a time constant of 37 s at 25 °C. Based on this, the
4.2. Carotenoids

Carotenoids are important pigments in photoregulatory systems of photosynthetic bacteria. They can either prevent the formation of highly destructive singlet oxygen by thermal dissipation of $^1\text{Chl}$[122–129] or quench the already produced singlet oxygen to its triplet ground state.[130] In higher plants, there are three carotenoid pigments that are active in the xanthophyll cycle: violaxanthin, antheraxanthin, and zeaxanthin (Figure 11). During light stress, violaxanthin is converted to zeaxanthin via the intermediate antheraxanthin, which plays a direct photoprotective role acting as a lipid-protective antioxidant and by stimulating non-photochemical quenching within light-harvesting proteins. Another role of carotenoids for photoprotective reaction is that they can directly quench already generated singlet oxygens. Due to the low-lying triplet excited state of the carotenoids, triplet carotene is formed as the singlet oxygen returns to its ground state.

The carotenoid photoprotection was successfully mimicked with a molecular system where a carotenoid moiety was covalently bonded to a porphyrin (Figure 12a).[131] Bleaching of diphenylisobenzofuran (DPBF), which is vulnerable to single oxygen, upon irradiating the aerated solution of the dyes were investigated. If the solution contains only a tetraarylporphyrin sensitizer in addition to DPBF, singlet oxygen is produced under illumination and rapidly reacts with DPBF, resulting in the fast bleaching of the dye. In the presence of the dyes I or II, a significant decrease in the rate of photodestruction of DPBF was observed because of the fast quenching of the triplet excited state of the porphyrin unit by the carotenoids, thus prevents the $\text{O}_2$ sensitization (Figure 12b).

Figure 10. Chemical structure of light intensity regulating pentad. Reproduced with permission from Ref. [121]. Copyright (2008) Nature Publishing Group.

Figure 11. Change in chemical structure of carotenoid pigments upon change in light intensity.

Figure 12. a) Chemical structures of carotenoporphyrin complexes. b) Bleaching of DPBF at 390 nm by singlet oxygen. Filled squares and circles are with I and II, respectively. Unfilled shapes represents multicomponent mixture of tetraarylporphyrin and $\beta$-carotene. Reproduced with permission from Ref. [131]. Copyright (1981) Nature Publishing Group.
5. Self-Healing

5.1. D1 Protein Repair Cycle in PSII

Despite the existence of photoprotective mechanisms in PSII, photodegradation occurs even at a very low irradiance. Several different mechanisms have been proposed for the PSII photodegradation; regardless of the mechanism, it is generally accepted that the irreversible photodamage of D1 protein is responsible for the photoinhibition of PSII. Once the D1 protein in PSII is irreversibly damaged by photons, a mechanism is activated where the damaged part of the PSII complex are replaced by a fresh one to restore the photochemical activity. Such a self-healing mechanism is termed as “PSII repair cycle”. Understanding the full cycles of self-healing is still underway, however, it has been assumed to consist of a number of distinct steps shown in Figure 13.

Figure 13. Schematic representation of PSII repair cycle. Reproduced with permission from Ref. [136]. Copyright (2011) The Royal Society of Chemistry.

In 2008, the Nocera group reported a preparation of Co-based electrocatalyst, namely Co-Pi, which is capable of performing water oxidation. They observed deposition of the catalyst upon the oxidative polarization of an inert indium tin oxide (ITO) electrode in Co(II) ion containing phosphate buffer. The catalyst was formed in situ and operated at low overpotential of 280 mV. Indeed, a plausible self-healing pathway was proposed in the paper. The catalytic system was further studied by the same group and the self-healing capability was confirmed. Leaching of cobalt was observed during the water electrolysis, while by applying potential in the presence of a phosphate counter ion resulted in a redeposition of the catalyst. It was noteworthy that the phosphate electrolyte ensures then the stability of the catalytic film, by promoting redeposition of Co(II), generated from electrochemical oxidation of Co(III) ions leached in solution (Figure 14). A very similar strategy with Co-Pi, MnO2 water oxidation catalytic was reported by Najafpour et al. Self-healing of a MnO2 electrocatalytic film in the presence of CeIV was demonstrated.

As an important step forward to artificial photosynthesis, Nocera’s self-healing WOC was further applied for a photoanode visible-light driven water splitting photoelectrochemical cells (PECs). Gamelin and co-workers reported a PEC where the photoanode was prepared by electrodepositing Co-Pi on the surface of photo-active hematite (α-Fe2O3) instead of using ITO as a substrate. Under AM 1.5 solar irradiation, the PEC showed reduction of the bias voltage (> 350 mV) for water splitting. Steinmiller and Choi reported another photoelectrochemical approach by photochemically depositing Co-Pi on ZnO rods. By irradiating UV light instead of applying external bias, photogenerated holes in the ZnO rods were used to oxidize Co(II) ions to Co(III) ions to precipitate the Co-based catalyst onto the surface. The photodeposition method ensures the deposition of the catalyst where the photogenerated holes are most readily available, thus provides optimal catalytic site for catalysis. In the presence of Co-Pi, the ZnO photoelectrode showed reduction of onset potential by 0.23 V with enhancement of anodic photocurrent observed in a wide potential range. In both systems by Gamelin and Choi, the leaching of the catalytic species was ruled out due to the self-healing ability of the Co-Pi catalyst, thus prolonged the catalytic activity. Since the reports, Co-Pi has been coupled with various light-active semiconductors to enhance the catalytic activity of a photoanode for O2 evolution, implying the importance of self-healing for prolonged and efficient catalysis.

By incorporating Co-Pi with a triple junction amorphous silicon (3jn-a-Si) photovoltaic cell and H2-evolving NiMoZn ternary alloy, a very high efficient solar-water-splitting device, namely “artificial leaf” was constructed with a device configuration of Co-Pi/3jn-a-Si/NiMoZn (Figure 15). Overall solar-to-fuels efficiencies (SFE) of 4.7% was recorded with the artificial leaf, corresponds to the overall water splitting efficiency of 60%.

The Bocarsly group reported a photoelectrochemical splitting of water in an ambient condition using polycrystalline CuRhO2 as a photocathode. It was proposed that the presence of O2 in the electrolyte solution either prevents the formation of metallic Cu or rapidly reacts with trace quantities of Cu to regenerate CuRhO2.

One implication on the organometallic catalysts is that they are prone to undergo ligand dissociation in the photolysis conditions. Eisenberg and co-workers showed regeneration of the ligand-dissociated catalysts by adding free ligand that reconstituted the catalyst. Photocatalytic H2 evolution kinetics of a cobalt catalyst, CoIII(dmgH)pyCl (where dmgH = dimethylglyoximate and py = pyridine) were compared with various concentrations of free dmgH (Figure 16a). In the absence of the free ligand, the H2 evolution ceased in 5 h with a turnover
of free ligand sometimes deteriorates catalytic activity when a metallic catalyst was used. The Bernhard group reported a photocatalytic H₂ production using Ir³⁺ (ppy)₂(bpy) (where ppy = 2-phenylpyridine and bpy = 2,2'-bipyridine) photosensitizers and colloidal Pt catalyst. Addition of 50 equiv free bpy ligand to the system lowered the H₂ production activity to 40% of its original activity instead of regenerating the Ir³⁺ photosensitizer, which was attributed to poisoning of the Pt catalyst.

Metal-organic frameworks (MOFs) have been studied as a scaffold for incorporating photosensitizers and catalysts for solar fuel production due to their high ordered structure, high porosity, and facile functionalization. Park and co-workers suggested using the MOF as a self-healing platform. A series of UiO-67-based MOFs, namely Pt₃-Ir-BulO₃, comprising 2,2'-bipyridine-5,5'-dicarboxylate (L) as a self-healing site, Pt⁴⁺(L)Cl₂ as a H₂-evolving catalyst, and Ir³⁺(ppy)₂(L) as a photosensitizer were synthesized and tested for photocatalytic H₂ production (Figure 17). Once the Pt-diimine bond was cleaved during HER, abundant L ligand promoted re-coordination of Pt to its diimine site and recovered the molecular catalytic activity. As a result, the catalysis prolonged more than 6.5 days, while the control MOF system without a free diimine ligand showed leaching of Pt to form colloids.

6. Summary and Outlook

The purpose of this Review has been to understand and benchmark the natural photosynthetic system and describe their incorporation into artificial photosynthesis. Towards this end, three important and unique strategies in PS II were stated: i) accumulative charge transfer, ii) photoprotection, and iii) self-healing. The natural photosynthetic system has been evolved to fulfill the strategies that the active units have optimal spatial positions in a protein matrix for the balance between efficient charge accumulation and photoprotective operation. Additionally, the damaged proteins can be replaced through a self-healing mechanism to further prolong the photosynthetic activity. Many challenges have been made as analogues for each strategy for artificial photosynthesis. Successful
achievements have been made using either supramolecular chemistry or an organic–inorganic hybrid approach. It was shown also in inorganic systems, that is, Nocera’s Co-Pi catalyst, that the microscopic approach on the molecular or atomic scale was very useful to control the catalytic activity.

The promising results reported so far provide a good blueprint for artificial photosynthesis; this research field requires further development for real life application. The current status in artificial photosynthesis is that each component responsible for light harvesting, charge transfer and accumulation, and catalysis can be optimized in different working conditions, however, combing them in a single device as a complete module is still a challenging task. Careful orchestration of the three strategies mentioned in this article in one system is required. In the integrated system we have to take account of critical factors:

1) Balancing between charge accumulation and the regulatory mechanism to aim to “kill two birds with one stone”, that is, keeping optimal solar fuel production efficiency while the stability is guaranteed under fluctuating solar irradiation;
2) Self-healing should work while the catalytic system is under operation;
3) The self-healing mechanism itself should be self consistent, not by stoichiometrically consuming other reagents or additivites.

Supramolecular chemistry can take a part to mimic the role of protein matrix in natural photosystem. Controlling charge separation, -transfer, and accumulation along with self-healing can be accomplished with a supramolecular approach. Combining the benefits of homogeneous and heterogeneous system can also provide a solution. The molecular system has merits of synthetic variety, ease of physical and chemical property tuning, high catalytic site accessibility, while the disadvantage of low stability and low conductivity can be solved by complementary inorganic systems. The multidisciplinary approach is still challenging, but we can learn from the 3.4 billion years of evolution in nature.

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Conflict of interest

The authors declare no conflict of interest.

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