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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 H_2 to an easily storable form, recent progress on storage of hydrogen as liquid or solid form has also been described in this article.

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Introduction

Photosynthesis is an important biological process by which plants and some bacteria utilize solar energy to produce ATP and NADPH for fixation of CO_2 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 CO_2, which has caused the green house effect on the earth [2]. Thus, the sustainable production of solar fuels, such as H_2 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]-hydrogenase and [FeFe]-hydrogenase enzymes [11,12] to drive H_2 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 The hydrogenase enzymes have been replaced by Pt nanoclusters [8,9].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 H_2 production to replace Pt nanoclusters by more earth-abundant materials [14,15••,16•,17•,18•].

Because H_2 gas is explosive and its volumetric energy density is quite low, low-cost, energy-efficient storage of H_2 as a liquid or solid form is definitely needed for stationary and portable applications in the H_2-delivery infrastructure, which is also described in this article [19•].

Biohybrids for H_2 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 H_2; both are oxygen-stable, and their standard redox potentials are similar (the E^0 of the $NADP^+/NADPH$ couple at $pH = 7$ is -324 mV, 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 μmol H_2 (mg chlorophyll)$^{-1}$ h^{-1} [22•,23].

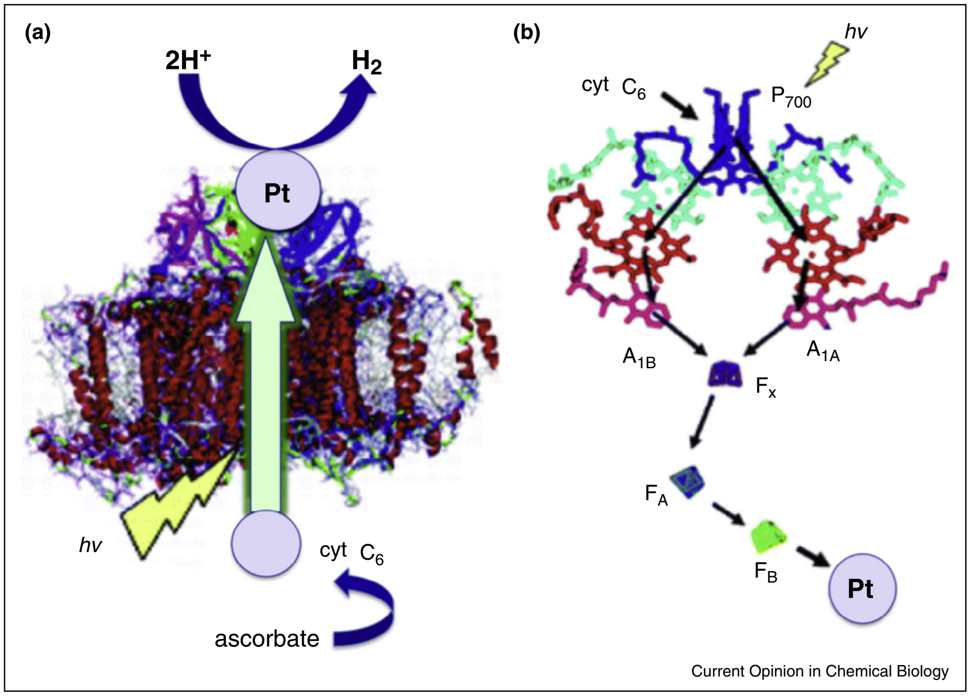
Hydrogenase can be replaced by Pt nanoclusters for the photocatalytic hydrogen production with PSI [24]. PtNPs bind readily to native PSI as shown in Figure 1a. The size of the nanoparticles was estimated to be 3.0 ± 0.2 nm [25]. PtNPs form a complex with PSI in a 1.0 ± 0.2 Pt nanoparticle/PSI monomer; 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 μmol H_2 (mg chlorophyll)$^{-1}$ 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 μmol H_2 (mg chlorophyll)$^{-1}$ h^{-1} [26,27].

[FeFe]-hydrogenase from *Clostridium acetobutylicum* (CaI) has also been combined with CdS nanorods (NRs) instead of PSI for photoinduced H_2 production using ascorbate as an electron donor with quantum yields (QY(H_2)) of up to 20% at a CaI:CdS NR molar ratio of 1:1, where QY(H_2) is defined as (H_2 molecules produced/photons absorbed) × (2 electrons/H_2 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 H_2, whereas holes are scavenged by the electron donor ascorbate (AscH$^-$) [28,29].

Inorganic photocatalysts for H_2 production

Both PSI and hydrogenases for photoinduced H_2 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 H_2 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 $k = 5.7\ (\pm 0.7) \times 10^9\ M^{-1}\ s^{-1}$) [33]. For hydrogen generation, two one-electron photochemical reduction steps of the cobalt(III) complex are needed along with hydride formation and protonation [33].

Figure 1



(a) Photocatalysis of PSI/Pt nanoparticle complexes. **(b)** Schematic representation of the cofactors involved in sequential electron transfer in PSI. Cytochrome c_6 (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.