



## Review

## Photochemical hydrogen generation with porphyrin-based systems



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## ABSTRACT

While its main current use is that of a feedstock in the chemical and petrochemical industry, molecular hydrogen can also be considered, in perspective, as an interesting energy carrier to be used in place of conventional fuels, e.g., in devices such as fuel cells. From this viewpoint, of particular interest would be the possibility to generate hydrogen from water splitting using a source of renewable energy such as solar light. This could represent, in principle, an inexhaustible, environmentally friendly energy source. In this review we summarize recent work on photochemical hydrogen evolution carried out with systems based on porphyrins or metalloporphyrins, either as photosensitizers or as catalysts. The systems discussed are varied including different levels of complexity, performance, and mechanistic insight. In general porphyrin molecules appear as a very promising class of photosensitizers for photocatalytic hydrogen production.

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**Abbreviations:** ADT, azadithiolate; bpy, 2,2'-bipyridine; C, concentration; CTAB, cetyltrimethylammonium bromide; DeAC, decylammonium chloride; EDTA, ethylenediaminetetraacetic acid; ET, electron transfer; Fc, ferrocene; GC, glassy carbon; GDH, glucose dehydrogenase; HEC, hydrogen evolving catalyst; HER, hydrogen evolution reaction; IR, infrared; LB, Langmuir–Blodgett; MOF, metal–organic framework; MV<sup>2+</sup>, methyl viologen dication; NAD<sup>+</sup>, oxidized nicotinamide adenine dinucleotide; NADH, hydrogenated nicotinamide adenine dinucleotide; NADPH, reduced nicotinamide adenine dinucleotide phosphate; Nf, Nafion<sup>®</sup> membrane; NMI, naphthalene monoimide; Nonidet P-40, (octylphenoxy)polyethoxyethanol; P, light-absorbing photosensitizer; PEC, photoelectrochemical cell; Poly(Glu), anionic L-glutamate polypeptide; prod, irreversible oxidation products of SED; PSA, pyrenesulfonic acid; PVA, polyvinyl alcohol; RGO, reduced graphene oxide; SCE, saturated calomel electrode; SDS, sodiumdodecyl sulfate; SED, sacrificial electron donor; TEA, triethylamine; TEOA, triethanolamine; TFA, trifluoroacetic acid; TOF, turnover frequency; TON, turnover number; TPPH, 5,10,15,20-tetrakis(4-(hydroxyl)phenyl)porphyrin; Triton N-101, polyethylene glycol nonylphenyl ether; Triton X-100, polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether; Tween-40, polyoxyethylenesorbitan monopalmitate; UV–vis, Ultraviolet–visible; WOC, water oxidation catalyst; ZnTPP, zinc tetraphenylporphyrin;  $\Phi$ , quantum yield;  $\Phi_{H_2}$ , quantum yield of hydrogen production;  $\Phi_T$ , quantum yield for formation of the excited triplet state.

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“Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. . . . Water will be the coal of the future”

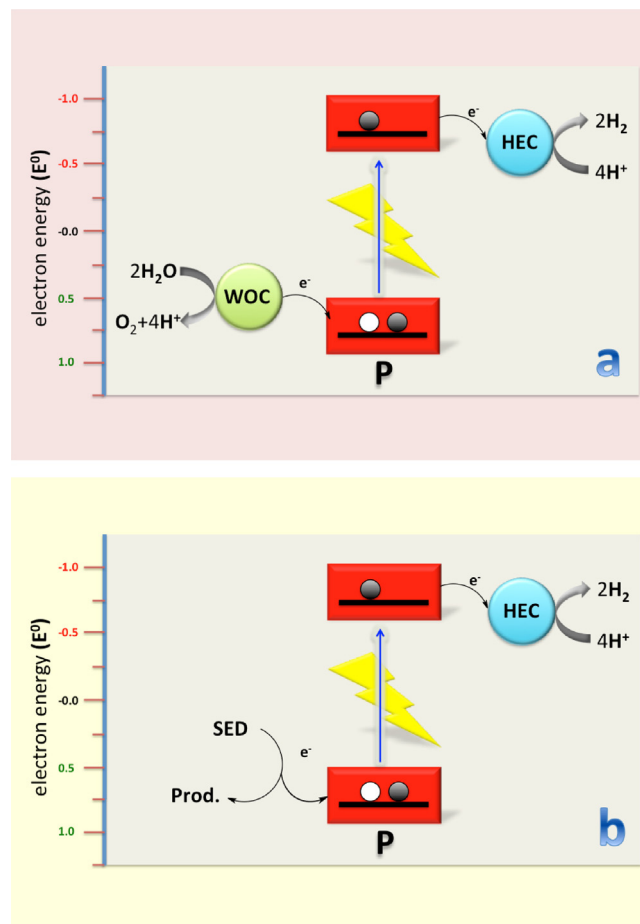
Jules Verne, *L'île Misterieuse* (1874)

## 1. Introduction

The interest in hydrogen as a synthetic fuel began to rise in the 1970s, about one century after the visionary statement by Jules Verne [1–3]. The main original motivation was the concern about depletion of oil reserves, but later on the problem of CO<sub>2</sub> emissions and anthropogenic global warming emerged as an additional, perhaps even more relevant issue. The idea behind the use of hydrogen as an energy carrier [4] is simple: (i) hydrogen is one of the most abundant elements on Earth; (ii) the combustion of molecular hydrogen with oxygen produces heat; (iii) the combination of molecular hydrogen and oxygen in a fuel cell generates electricity and heat; (iv) the only byproduct of such energy-producing processes is water. Therefore, if hydrogen could be produced from water cleanly, using a source of renewable energy, both the energy and the environmental problems of our planet could be solved [5–7]. Among the available renewable energy sources, solar energy is evidently the most attractive one because of its abundance, even distribution, and accessibility (the problem of intermittency is automatically solved by conversion into a fuel). Although hydrogen can in principle be produced by solar energy in an indirect way, i.e., by solar photovoltaics coupled with water electrolysis, direct photoelectrochemical conversion of solar energy into hydrogen by water splitting (“artificial photosynthesis”), though challenging, is by far more attractive.

A simplified scheme with the minimum set [8] of components required for photochemical water splitting is shown in Fig. 1a. The first essential component is a light-absorbing chromophore, usually called photosensitizer (P). The excited state, with its high-energy electron and low-energy hole, can accomplish water splitting in either of two ways, water reduction followed by water oxidation or vice versa. Water splitting being endoergic by 1.23 eV, many dyes absorbing visible light (1.5–3.1 eV) have, in principle, the thermodynamic power to perform this photochemical reaction [9]. The main problems to be faced, however, are of kinetic nature and pertain to the fact that, while the charge separation (and recombination) steps initiated by light absorption are fast one-electron processes, oxidation and reduction of water are intrinsically slow, multi-electron processes. Therefore, essential additional components of any water splitting photochemical cycle are multi-electron catalysts, able to store electrons or positive charges produced by the photosystem and to deliver them to the substrate in low activation energy processes. A large amount of research activity is currently being devoted to the development of efficient water oxidation (WOC) [10] and hydrogen evolving (HEC) catalysts [11–14].

Since the entire water splitting process is complex, with the efficiency limited by several possible shortcuts and charge recombination processes, a convenient strategy to facilitate the study and optimization of sensitizer and catalysts is to isolate one of the half-reactions by providing the charges required on the opposite side with a sacrificial redox agent, i.e., a species that following electron transfer undergoes some rapid reaction making the whole process irreversible. A half-cycle of this kind for the hydrogen generating reaction is shown in Fig. 1b. Convenient sacrificial electron donors (SED), frequently used in this type of experiment, are aliphatic amines, thiols, and ascorbic acid. Analogous schemes for the water oxidation reaction can be easily conceived, using sacrificial electron acceptors (SEA) (as, e.g., persulfate or Co(II) amine complexes).



**Fig. 1.** (a) Simplified scheme for a photochemical water splitting system: P = light-absorbing photosensitizer, WOC = water oxidation catalyst, HEC = hydrogen evolving catalyst; (b) sacrificial half-cycle for photochemical hydrogen evolution: SED = sacrificial electron donor, prod = irreversible oxidation products of SED.

In principle, once each side is optimized in sacrificial cycles, the two half reactions should be combined together in a regenerative system. Among possible coupling strategies, heterogenization onto electrodes and assembling of the full system as a photoelectrochemical cell (PEC) seems to be the most promising one [15–17].

As far as the hydrogen evolving catalysts are concerned, both heterogeneous and homogeneous systems have been used [18]. The most widely used heterogeneous HEC has been, somewhat obviously, platinum metal, usually in the form of colloidal particles in solution [19–22] or supported on various types of materials [23,24]. As alternative heterogeneous HECs, not containing noble metals and thus more suitable for application, NiMoZn alloys [25] as well as Mo and W sulfides [26,27] have also been considered. As to molecular HECs for use in homogeneous solution, a substantial amount of work has been performed using dithiolate bridged di-iron complexes, a class of catalysts inspired by the structure and function of [2Fe2S] natural hydrogenases [28–30]. Along with some Ni phosphine complexes [31], the other main class of molecular catalysts used in photochemical hydrogen evolution studies has been that of macrocyclic cobalt complexes, with molecules of the cobaloxime type playing by far the major role [32–35]. Notably, some work has also been performed using cobalt porphyrins and related structures as HECs (vide infra).

As far as photosensitizers for hydrogen evolution are concerned, both inorganic and organic dyes have been widely used. Among the inorganic species Ru(II) polypyridine complexes, with the prototype Ru(bpy)<sub>3</sub><sup>2+</sup> [36], have played by far the major role, although

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