



## Review

# Recent progress in homogeneous multielectron transfer photocatalysis and artificial photosynthetic solar energy conversion



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## ABSTRACT

As a consequence of global population growth, our modern civilization is facing many upcoming challenges such as gradually depleting energy resources, anthropogenic climate change and other serious environmental issues. In this context, the development of artificial photosynthetic systems for solar energy harvesting and sustainable fuel production represents one of the most attractive long-term strategies to address these important topics. Despite the indisputable benefits, which such a man-made counterpart of the biological solar energy conversion and storage machinery could provide, progress in mimicking the essential functions of natural photosynthesis still remains quite difficult to achieve. While ongoing efforts in replacing the light-harvesting and charge separation function of natural photosystems have led to some remarkable success, many aspects of powering the endergonic chemical reactions required have to be much further elaborated. The current limitations of most artificial photosynthetic systems are related to an inefficient coupling of the catalytic steps necessary for chemical bond formation and for an accumulation of energy rich product molecules (solar fuels). In the present review, some recent breakthroughs in these directions are briefly discussed.

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## 1. Introduction

Turning photons and abundant feedstocks into fuels by mimicking the light-dependent functions of green plants has been a central goal of photochemical research for more than a century [1]. Despite the enormous efforts in this direction, many of the

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**Table 1**  
Artificial and natural photosynthetic transformations and their thermodynamics<sup>a</sup>.

Energy storing (endergonic) reaction	$ne^-$	$\Delta G^\circ$ (kJ/mol)	$\Delta G^\circ$ (eV) <sup>b</sup>	$\lambda_{\text{thr}}$ (nm) <sup>b</sup>
$2 \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$	2	355	1.84	674
$2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$	4	475	1.23	1008
$2 \text{H}_2\text{O} + 2 \text{NAD}^+ \rightarrow 2 \text{NADH}/\text{H}^+ + \text{O}_2$	4	436	1.13	1098
$\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3/2 \text{O}_2$	6	701	1.21	1025
$\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_4 + 2 \text{O}_2$	8	818	1.06	1170
$6 \text{CO}_2 + 6 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$	24	2880	1.24	997

<sup>a</sup> Adopted from Refs. [3,4]

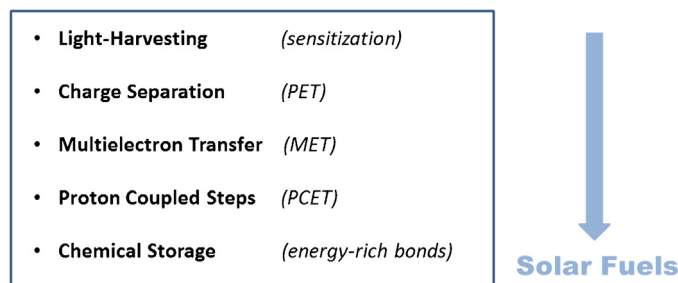
<sup>b</sup> Calculated per electron transferred.

fundamental aspects of such a process still remain to be discovered. Oxygenic photosynthesis is a sunlight-driven enzymatic reaction sequence which directly converts carbon dioxide and water into food and biomass. Sugars such as glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) are the typical energy-rich storage chemicals produced by natural photosynthetic carbon fixation. For every glucose molecule formed, 24 electrons and protons (2 hydrogen equivalents or  $4e^-/4\text{H}^+$  per assimilated  $\text{CO}_2$  molecule) have to be released from  $\text{H}_2\text{O}$  acting as a reductant (“sacrificial donor”). The thermodynamic constraints for powering such a process [2,3] require to capture the energy of 24 photons with a maximum threshold wavelength  $\lambda_{\text{thr}}$  of around 1000 nm (Table 1), which would then correspond to 100% efficiency of solar energy conversion into carbohydrate fuel. Natural oxygenic photosynthesis, however, where two photosystems (PS I and PS II) have been coupled in a row, requires capturing the energy of at least 48 red-light photons of about 680 nm (1.8 eV) in order to produce one molecule of glucose, which considerably reduces the theoretical maximum energy-storage efficiency to about 30% [4]. For polychromatic irradiation with sunlight, this value further drops to a theoretical limit of 12% [5], and plants can usually achieve no more than 5–6% solar power to carbon-based fuel conversion efficiency under optimum growth conditions [6]. Nevertheless, more than 80% of the current world energy supply are covered by burning the chemicals formed in the course of natural photosynthesis.

In an artificial photosynthetic system, many useful energy storage molecules other than carbohydrates could be produced. Instead of the net 24 electron process required for glucose production, several more easily accessible solar fuels such as alkanes, methanol or hydrogen would require a much less demanding level of multi-electron catalysis. Some alternative photosynthetic reactions are listed in Table 1. It should be pointed out, however, that for all of these examples the initial extraction of reduction equivalents ( $2e^-/2\text{H}^+$  or  $\text{H}_2$ ) from  $\text{H}_2\text{O}$  is the energetically limiting step. Therefore, one of the major challenges in the field of artificial photosynthesis is to achieve an efficient water oxidation reaction driven by photons in the long-wavelength region of the solar spectrum.

## 2. Modelling the key-steps of natural photosynthesis

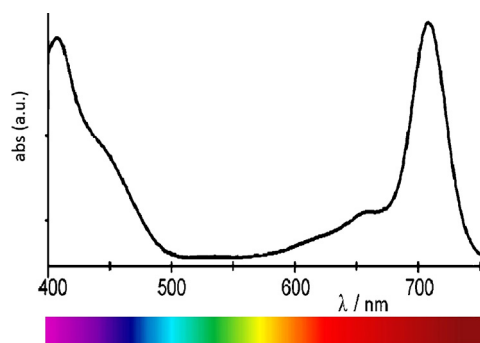
From a chemical perspective, natural photosynthesis is an endergonic photocatalytic redox reaction, which has been optimized for the conversion of far-red light photons into chemical energy. The basic functional requirements of such a process can be rationally analysed [7] and these considerations may serve as a starting point for the development of fully operating artificial photosynthetic devices. Such an ambitious endeavour, however, requires a perfect coupling of all building blocks to orchestrate the necessary key-steps ranging from fundamental photophysical processes to light-mediated redox chemistry and biomimetic catalysis [2,7,8]. The state of the art of modelling these individual steps, which are summarized in Scheme 1, will be briefly discussed in the following sections.



**Scheme 1.** Basic functional requirements for the construction of photosynthetic model systems.

### 2.1. Light-harvesting and energy transfer

The first step in solar energy conversion is light absorption. Light-harvesting complexes in photosynthetic antenna systems contain a set of specialized pigments including chlorophylls strongly absorbing in the long-wavelength part of the visible spectral region and beyond (Fig. 1). These pigments are acting as photosensitizers to transduce their excitation energy to the photochemically active reaction centres. The reaction centres of oxygenic photosynthetic organisms are operating near the red-edge of the solar spectrum at around 680 nm (PS II) and 700 nm (PS I). Any excess energy of light absorbed at shorter wavelengths is converted to heat. Modelling the spectroscopic features of the natural light-harvesting chlorophyll pigments with robust synthetic compounds is an important task for the construction of artificial photosynthetic devices [2,8]. It is remarkable, that the long-wavelength limits of photochemical energy conversion in different photosynthetic organisms have only recently been found to extend significantly into the far-red region of the solar spectrum [9–11]. Such an extended threshold wavelength region closer to the absolute thermodynamic limits (Table 1) should also be considered as a benchmark value for synthetic light-harvesting chromophores. While many photosensitizers investigated in the field of artificial photosynthesis are still absorbing at much shorter wavelengths, several alternative dye molecules with a longer



**Fig. 1.** Absorption spectrum of the far-red light harvesting chlorophyll Chl f [9].

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