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Solar-driven proton and carbon dioxide reduction to fuels — lessons from metalloenzymes

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Metalloenzymes such as hydrogenases and carbon monoxide dehydrogenase can be attached to light-harvesting agents to produce informative photocatalytic systems of varying intricacy. Systematic studies yield important insight into mechanistic and design principles of artificial photosynthesis – one route to future renewable energy conversion, and the unconventional experiments reveal interesting new criteria for the catalytic performance of metals in biology. Recent advances are interpreted in terms of the importance of enzyme active centres that have evolved to perform fast and efficient catalysis using abundant elements, along with the ability of enzymes to trap photo-generated electrons by virtue of having receding, buried relay centres with low reorganisation energies.

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Introduction

Defined most loosely, Artificial Photosynthesis (AP) means using solar energy to make fuels without a living organism. This Opinion focuses on a specific concept — the role of metalloenzymes in enhancing the development of integrated chemical systems that constitute an ‘artificial leaf’.

Building on the principles of natural photosynthesis, light absorption and accompanying charge separation (using semiconducting materials instead of biological pigments) is coupled, simultaneously, to two complex endoergic reactions — oxidation of water to O_2 and reduction of water or CO_2 into energy-rich products. The latter can be fuels such as hydrogen or carbon-based molecules (‘solar fuels’) or valued organic chemicals (‘solar chemicals’). Whereas solar electricity (photovoltaics) is mature technology, AP is still in its infancy and systems rarely possess efficiencies above 5% (notable exceptions are given in references [1–5]). What are often referred to as ‘*co*-catalysts’ have a special role in improving this efficiency — the issue being that few synthetic compounds are recognised to be fast, efficient *electro*catalysts for water oxidation or H^{+}/CO_2 reduction. In contrast, certain redox enzymes, particularly those acting on H_2 and CO_2, rank among the most efficient of all electrocatalysts [6•]. Studies by protein film electrochemistry (PFE), where the enzyme is attached directly to an electrode surface, have established turnover frequencies (TOF) exceeding $10^3\ s^{-1}$, with minimal driving force (overpotential) requirements [7•,8,9]. These outstanding electrocatalytic properties suggest that enzymes have an important place in AP development, not directly in technology, but to guide concepts and design strategies.

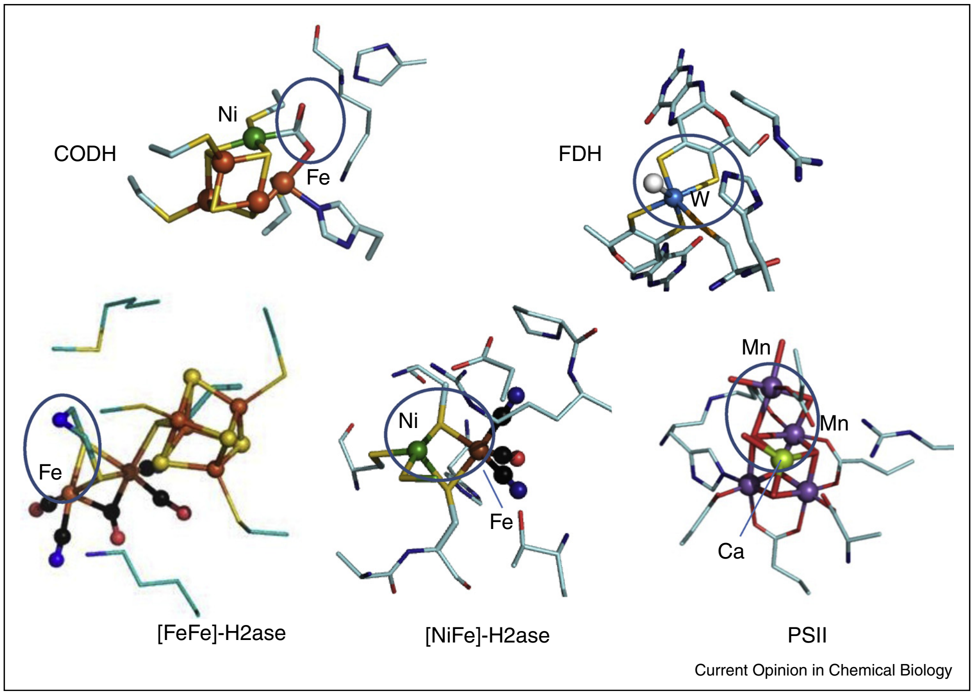
Enzyme efficiency was perfected long ago by molecular evolution: catalytic redox conversions involve highly organised proton-coupled electron transfers (PCET) at active sites that are buried and shielded from disruptive solvent molecules whose entry is tightly controlled. Figure 1 depicts active sites of metalloenzymes immediately relevant to AP systems: second metals (where relevant) and all the ancillary (second and outer shell) atoms are optimally positioned. Additionally, redox enzymes possess specialised electron-transfer centres such as FeS clusters, also buried, that provide fast internal ‘wires’ and electron traps [6•]. All this is achieved with earth-abundant elements — demonstrating what is possible *without* rare or expensive elements, a crucial issue discussed recently by Thoi *et al.* [10•].

The case for using enzymes in artificial photosynthesis systems

H_2 production

The active sites of hydrogenases (H2ases) rival Pt in performance [11], and both main classes of enzyme, [FeFe]-H2ases and [NiFe]-H2ases [12•,13•], have been incorporated into integrated AP systems. Although [FeFe]-H2ases are more active H_2 producers, they are inactivated irreversibly by trace O_2 [12•]. The [NiFe]-H2ases are less sensitive to O_2 and some even function in air, but they are less active H_2 producers, partly because H_2 binds tightly and is a strong inhibitor. One exception is the subclass known as [NiFeSe]-H2ases: these enzymes, in which one cysteine ligand to Ni is replaced by selenocysteine, are excellent H_2 producers that retain some activity in the presence of O_2 [14].

Figure 1



Active sites of enzymes catalysing the reactions relevant to artificial photosynthesis with very high rates and efficiencies. Regions considered to be at the focus of the catalytic transformation are indicated by ovals. Note the specifically positioned groups outside the inner coordination shells, and the mineral-like oxido structure of the oxygen evolving centre of PSII. Generated in PyMOL using the Protein Data Bank structures, 3C8Y, 3USC, 3B52, 3ARC and 1HOH.

CO_2 reduction

Two classes of enzyme, carbon monoxide dehydrogenases (CODH) and formate dehydrogenases (FDH), catalyse two-electron reduction of CO_2, the first and crucial stage of its entry into organic chemistry. The enzymes avoid radical intermediates such as CO_2^- or COOH (−1.9 V *vs.* SHE at pH 7 [15•]) proceeding instead *via* PCET in single concerted steps to CO or HCOOH. Both CODH and FDH are reversible electrocatalysts when attached to graphite electrodes [8,16], suggesting their potential as CO_2 reduction catalysts in (bench-scale) AP systems. The supremacy of CODH over metal electrocatalysts inspired an interesting comparison by Nørskov and co-workers [17••], who argued the importance of the active site of CODH being able to attack CO_2 at *two* atoms (Ni–C and Fe–*departing* O) simultaneously, stabilising a bound intermediate without also stabilising bound CO.

Water oxidation

The unique, mineral-like [4MnCa-5O] active site of photosystem II (PSII) [18–20] is the benchmark for oxygen evolution reaction (OER) catalysts. The enzyme operates at neutral pH with TOF >100 s^{-1}, whereas most electrocatalysts require acidic or basic media for efficient operation, along with a sizeable overpotential [21]. The turnover number is limited to about 10^6 because subunit D1, which supplies most of the ligands to the [4MnCa-5O] cluster, is damaged by intense photocatalytic activity and replaced every 25 min [22,23]. Herein lies a lesson for AP, because outside biology there is no automatic repair mechanism for oxidative damage: a useful synthetic OER catalyst must therefore be stabilised under oxidising conditions and avoid organic ligands. The robust Co and Ni oxide catalysts developed by Nocera and co-workers are good examples of heeding this rule [24,25•].

Although PFE studies of PSII are limited compared with H2ase and CODH, the enzyme displays *photoelectro*catalysis when interfaced with different nanomaterials [26] — the light-harvesting and catalytic components being inseparable parts of the same super-molecule. Recent reports include O_2 evolution by His-tagged PSII immobilised on Au-nanoparticles [27], using mesoporous indium-tin oxide electrodes for direct and mediated electron transfer (ET) [28], covalent anchoring [29], and incorporation into redox-active polymers [30–32]. Enzyme-based photovoltaic cells have also been devised [33,34].

Common mechanistic principles?

Billion years of evolution have perfected the ability of the redox-enzymes depicted in Figure 1 to carry out