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Designing artificial photosynthetic devices using hybrid organic–inorganic modules based on polyoxometalates

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Artificial photosynthesis aims at capturing solar energy and using it to produce storable fuels. However, while there is reason to be optimistic that such approaches can deliver higher energy conversion efficiencies than natural photosynthetic systems, many serious challenges remain to be addressed. Perhaps chief among these is the issue of device stability. Almost all approaches to artificial photosynthesis employ easily oxidized organic molecules as light harvesters or in catalytic centres, frequently in solution with highly oxidizing species. The ‘elephant in the room’ in this regard is that oxidation of these organic moieties is likely to occur at least as rapidly as oxidation of water, meaning that current device performance is severely curtailed. Herein, we discuss one possible solution to this problem: using self-assembling organic–polyoxometalate hybrid structures to produce compartments inside which the individual component reactions of photosynthesis can occur without such a high incidence of deleterious side reactions.

1. Introduction

As global demand for energy continues to grow, the need for renewable, carbon-neutral energy sources becomes ever greater [1]. Currently, the main globally distributed renewable energy sources (wind, solar, hydro and tidal

power) only produce *electricity*, and (with the exception of hydropower) do so only intermittently. This presents the problem of energy storage for mobile applications and for times when the Sun is not shining or the wind is not blowing. A specially attractive way of achieving this energy storage is to use renewable energy inputs to effect the formation of chemical bonds, to make fuels that can be stored safely and used when required [2,3]. Of all renewable energy sources, solar power is by far the most abundant: roughly 120 000 TW of solar power hits the surface of the Earth each year (or about 8500 times the amount of power that the human race currently uses per annum [1,4]). This equates to an Earth's-surface average insolation of around 200 W m^{-2} , other geographical factors notwithstanding [5], meaning that solar irradiation is a fairly diffuse, low-power resource. In this regard, natural photosynthesis is unique in being the only major extant chemical process capable of producing fuels directly from solar energy [6]. While direct use of photosynthesis in the production of biofuels (e.g. in the conversion of the photosynthetic product sucrose into ethanol [7]) has attracted increasing interest in recent years, efficiency and pressures on agricultural land remain problematical. Indeed, while some microalgae grown in small bioreactors are capable of converting 5–7% of the Sun's energy into biomass [8], the vast majority of crops have efficiencies below 1 per cent [9]. Hence, in order to produce even a small fraction of the biofuels required to meet existing demands, significant amounts of land will have to be given over to fuel production, at the expense of cultivating crops for food [10]. It is for these reasons that routes to abiological, *artificial* photosynthetic systems (capable of harvesting the Sun's energy and turning it into fuels) are actively sought [11].

2. The basics of artificial photosynthesis

The basis of natural photosynthesis is the removal of electrons from water (using solar irradiation as the energy input), which are then used to reduce atmospheric carbon dioxide to carbohydrates [12]. The aims of artificial photosynthesis are similar, although the desired end product could be any of a range of suitable fuels. The four key steps in the operation of an idealized artificial photosynthetic device are shown in figure 1.

Step 1 involves capturing the energy of solar irradiation, or 'light harvesting'. This energy input serves to create oxidizing equivalents (step 2), which are then used to oxidize water (step 3). This liberates both protons and electrons, which can subsequently be used to reduce carbon dioxide to storable fuels such as methanol.

Light harvesting is generally performed by one of two methods: either the light is absorbed by a dye molecule (as in natural photosynthetic systems), or else the harvesting is performed by an external device, such as a silicon photovoltaic array. Arguably, the second approach is preferable, on account of the high conversion efficiency for solar into electrical energy obtained with standard silicon-based solar cells (typically 10–20%) [5]. The challenge then becomes how to interface between the photovoltaic and a catalyst capable of performing water oxidation. Very recently, Reece and Nocera and co-workers demonstrated just such a device (the 'artificial leaf') capable of splitting water into hydrogen and oxygen when illuminated with visible light [13]. Most impressively, neither of the (heterogenous) oxygen or hydrogen-evolving catalysts used in this work contained any precious metals. Moreover, the system contains no organic components, and so there is no risk of oxidizing these in competition with water oxidation.

In contrast, approaches that rely on organic dyes to perform the light harvesting must separate the dye from the water-oxidation catalyst if even mediocre system stability is to be attained. Indeed, at the potentials necessary to oxidize water, most organic compounds will be oxidized at least as quickly as water is: even in photosystem II (PSII), oxidative damage to the protein matrix sustained during water oxidation at the reaction centre requires the entire ensemble to be replaced every half hour or so [14]. This suggests a need to develop artificial photosynthetic systems where the highly oxidizing water-oxidation catalyst is isolated from any organic light-harvesting apparatus, and where interactions between any organic moieties and the water-splitting reaction centre are limited. These requirements will be discussed in more detail with reference to functional water-splitting molecules in the next section.

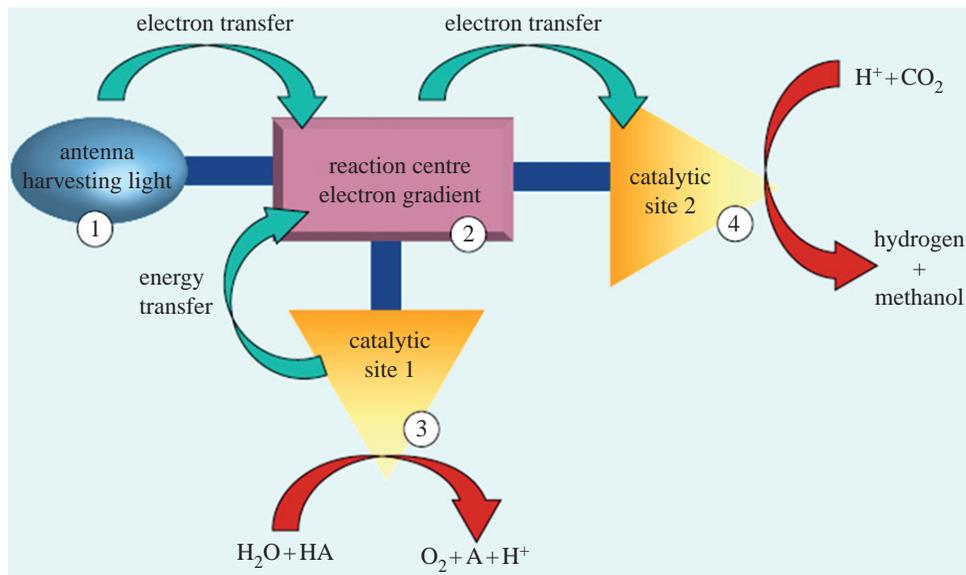


Figure 1. Schematic of the photosynthetic process. Module 1 is a light-harvesting device that funnels energy into the reaction centre. In natural photosynthetic organisms, this module equates to the antenna proteins. Module 2 then uses this incoming energy to separate charges, which are used in Module 3 to remove electrons from a suitable substrate, typically water. In plants, this function is performed by the oxygen evolving complex present in PSII. The electrons and protons thus produced are used in Module 4, where reduction of a suitable substrate occurs. This substrate could be either protons (forming H_2) or CO_2 to form (e.g.) methanol. (Online version in colour.)

3. Compartmentalized artificial photosynthesis

The limitations on homogeneous artificial photosynthetic systems raised in the previous section can be mitigated to some extent by localizing the reactive components to specific areas, and thus isolating them from each other. Natural photosynthetic systems achieve this through anchoring the relevant enzymes in membranes [6]. Recently, our group demonstrated the formation of organic–inorganic hybrid tubes [15–17] and membranes [18], which form spontaneously when crystals of polyoxometalates [19] are immersed in solutions containing sparingly soluble cations. Although these structures are of micro-scale dimensions, the direction of growth of the tubes can be controlled macroscopically by judicious application of a heat gradient [16], while the tube diameter is also easily regulated [17]. Moreover, these structures are hollow, and can act as pipelines for other reagents. Figure 2 gives some idea of the directional control possible with these tubes and their dimensions.

Of particular interest to artificial photosynthetic systems are the membranous structures that can be prepared by these techniques [19]. Dubbed inorganic chemical cells (iCHELLs), these structures can be made to incorporate redox-active or chiral constituents, or they can be made to incorporate an iCHELL of different composition ‘nested’ within them. Figure 3 demonstrates the nested growth of one iCHELL within another of different composition both schematically and with time-lapse photography. Furthermore, iCHELLs can be produced reliably in large numbers using microfluidic techniques, making these systems attractive for use as ‘capsule’ catalysts that can selectively import reagents and sense the exterior environment.

One of the key assets of these tubular and membranous structures is that they form with a wide range of polyoxometalate anions and organic cations. This is especially relevant to the current discussion, as both structural [20] and functional [21,22] polyoxometalate-based analogues of the water-oxidizing reaction centre of PSII have recently come to light. The structure of the latter is shown in figure 4a and has a central $\{\text{Mn}_5\text{-oxo}\}$ fragment that can be regarded as a

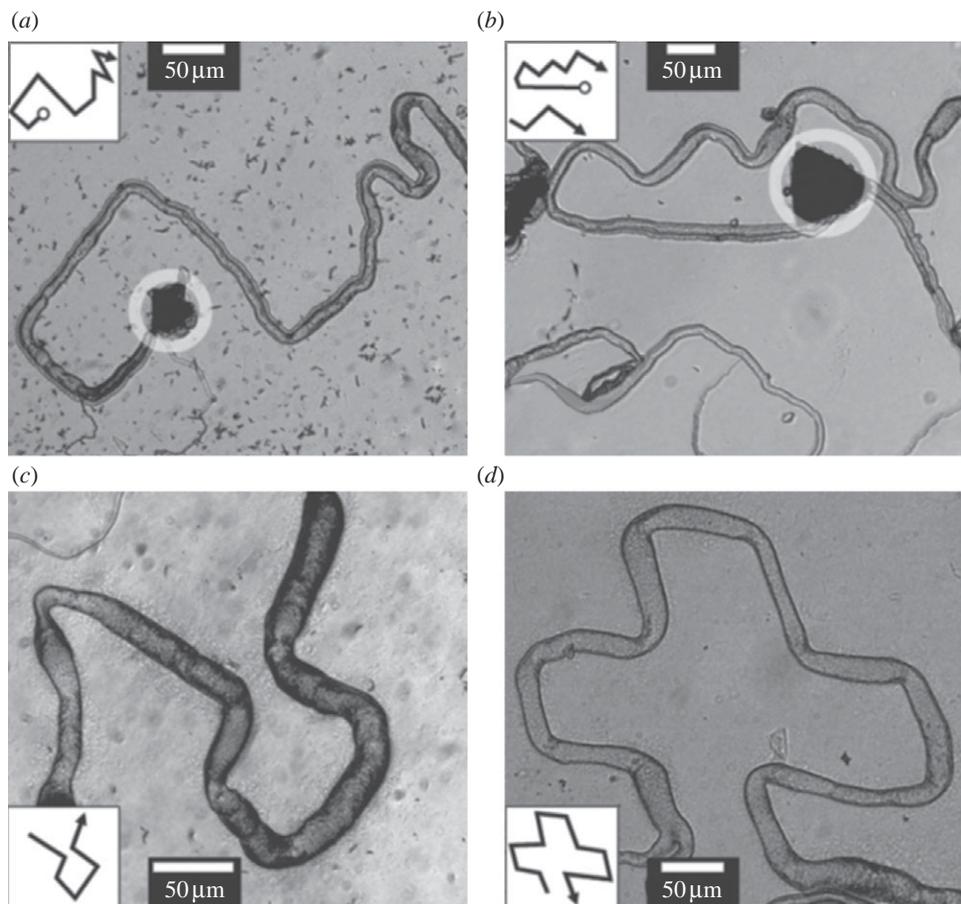


Figure 2. Examples of the controlled growth of polyoxometalate–organic hybrid tubes. By careful application of an electric field (which gave rise to a heat gradient in the solution in which the tubes were growing), various motifs could be ‘drawn’. (a) 90° bends followed by a series of 180° turns. (b) A series of 90° bends to make a zigzag motif. (c) 90° bends to form a square. (d) A series of 90° turns making a cross-shape. Circles indicate the crystals from which the tubes are growing. The smaller inset diagrams give an overall indication of the direction of the tube growth.

{Mn₄O₄} cubane attached to a ‘dangling’ Mn(II) centre via one of the oxygen atoms of the cube. The entire {Mn₅-oxo} unit consists of three Mn(II) and two Mn(III) centres, where three μ₃-O²⁻ anions, two μ₂-O²⁻ anions and one μ₄-O²⁻ anion act as ligands. This cubane-plus-dangler arrangement is highly reminiscent of the {Mn₄-oxo} cubane found in the proposed structures for the active site of PSII [23–25]. Figure 4*b* shows the structure of a polyoxometalate-based functional analogue of the water-oxidizing reaction centre of PSII. This wholly inorganic water-oxidation catalyst was reported independently by the groups of Bonchio [22] and Hill [21] and features a tetra-ruthenium(IV)-oxo core stabilized by {γ-SiW₁₀} polyoxotungstate ligands.

Bonchio and co-workers demonstrated the competence of this scaffold for water oxidation by first oxidizing the polyoxometalate with Ce(IV) in aqueous solution, and then monitoring the oxygen evolved as the oxidized polyoxometalate in turn oxidized water. Turnover numbers of over 450 h⁻¹ were reported by this method. In contrast, Hill and co-workers used the tetra-ruthenium polyoxometalate in conjunction with the oxidant [Ru(bpy)₃]³⁺ (bpy = 2,2′-bipyridine) to effect water oxidation. This is important with regard to artificial photosynthesis, as [Ru(bpy)₃]³⁺ is generated from [Ru(bpy)₃]²⁺ when the latter is irradiated with visible light in the presence of a suitable electron acceptor. Hence, light-driven water oxidation should be

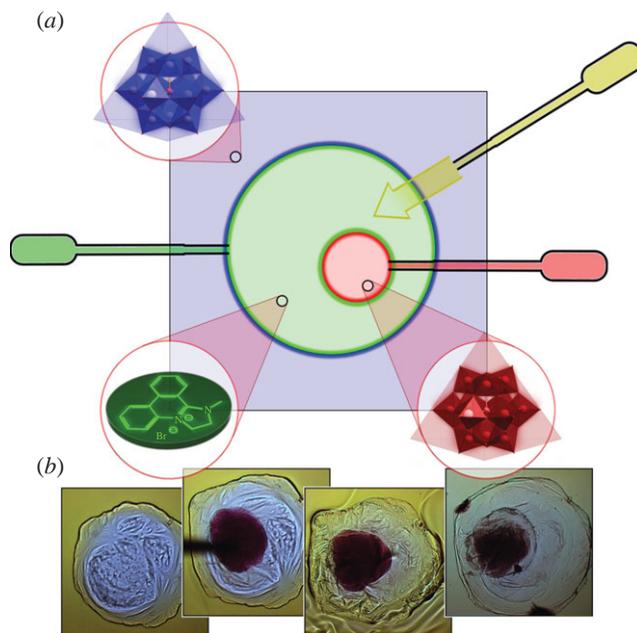


Figure 3. (a) A schematic of one iCELL being grown inside another. A salt solution containing a large organic cation (left-hand side) is injected into a salt solution containing a large polyoxometalate anion (square box), giving rise to a membrane. A second polyoxometalate-containing solution that is different from the first (right-hand side, lower) is then injected into the first cell, producing a second membrane. Addition of an external reagent (right-hand side, upper) then causes a reaction in the inner cell after a certain time interval governed by diffusion. (b) Time-lapse images showing the growth of an iCELL in phosphomolybdic acid, followed by the construction of a second phosphotungstic acid-based iCELL inside the first iCELL. The phosphotungstic acid iCELL was made to contain potassium permanganate and when hydrogen peroxide solution was added to the space between the two iCELL membranes, discoloration of the inner permanganate-containing iCELL was observed after a few minutes. (Online version in colour.)

possible with such systems. However, it must be stated that the organic bipyridines present on the co-catalyst ($[\text{Ru}(\text{bpy})_3]^{3+}$) in the report from Hill and co-workers do seem to suffer from some oxidative degradation during water splitting, as alluded to previously. This is borne out both by the loss of $[\text{Ru}(\text{bpy})_3]^{3+}$ co-catalyst (only 90% of the reduced form could be recovered, suggesting 10% degradation of the co-catalyst), and in the lower than expected yield of O_2 (only 66% of that predicted based on the amount of co-catalyst used). The most probable explanation for these losses is undesired oxidation of the organic moieties present, giving CO_2 and other oxidized carbon species. This is by no means a problem restricted to the system under discussion: organics are always likely to be oxidized at a comparative rate to water at the potentials where water oxidation occurs. Hence, the challenge is to try to minimize the organic content of such systems, or to try and protect the organic components by spatial isolation from the water-oxidizing centres.

With regard to the foregoing discussion, it would seem that an approach based on tubes or iCELLs grown using the tetra-ruthenium polyoxometalate of Bonchio and Hill in combination with a suitable dye, could be a suitable candidate for a compartmentalized water-oxidation centre in an artificial photosynthetic device. The ability of such structures to essentially self-assemble from solution would be a tremendous asset in terms of the simplicity of their construction, and also in terms of their removal and replacement in the case of oxidative damage. Hence, one aim could be to use a $[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4]^{6+}$ core within a polyoxometalate anion in conjunction with oxidation-resistant dyes as the counter-cations, to produce self-assembling membranes competent for light-driven water oxidation. Work towards this is currently underway in our laboratories.

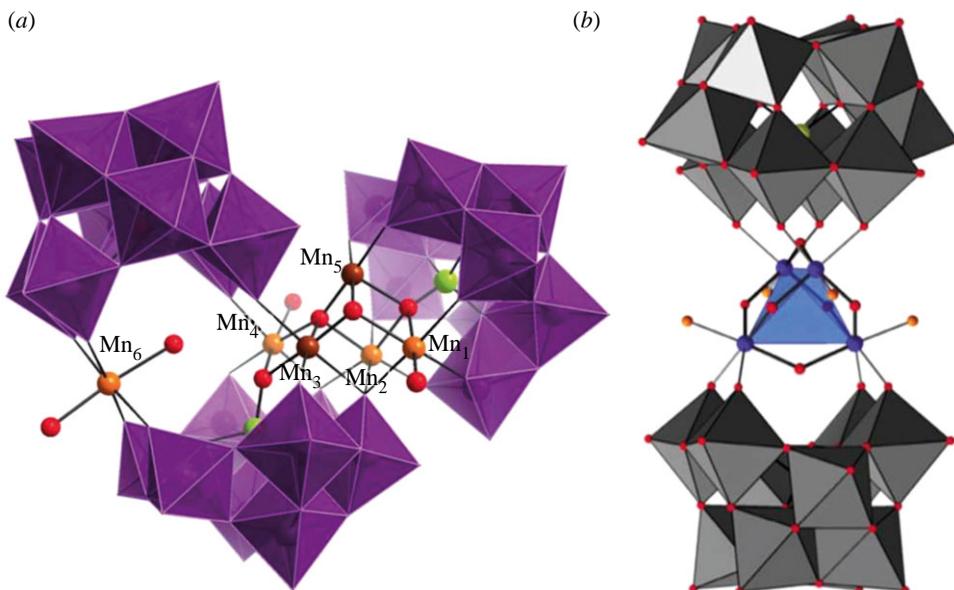


Figure 4. (a) The structure of a polyoxometalate-based structural analogue of PSII, $[\text{Mn}_2^{\text{III}}\text{Mn}_4^{\text{IV}}(\mu_3\text{-O})_2(\text{H}_2\text{O})_4(\text{B-}\beta\text{-SiW}_8\text{O}_{31})(\text{B-}\beta\text{-SiW}_9\text{O}_{34})(\gamma\text{-SiW}_{10}\text{O}_{36})]^{18-}$ showing the three inequivalent silicotungstate Keggin fragments and the appended $[\text{Mn}_4\text{O}_4]$ cubane core with a 'dangling' Mn ion very similar to that found in the structure of PSII. WO_6 units are shown as polyhedra and Mn centres are labelled. Potassium and solvent water molecules have been omitted. (b) Ball-and-stick structure of the $[\text{Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4]^{6+}$ -containing functional analogue of PSII reported by Hill and co-workers (hydrogen atoms omitted for clarity) with the slightly distorted $\{\text{Ru}_4\}$ tetrahedron highlighted in the centre of the structure. The polyoxotungstate supporting ligands are shown in polyhedral representation. (Online version in colour.)

4. Challenges for the future

The generation of oxidation-resistant and light-driven water-oxidizing membranes would be a major advance in molecular approaches to artificial photosynthesis. However, even more challenging than such studies is the coupling of the protons and electrons produced during water oxidation to the reduction of carbon dioxide. In natural photosynthetic systems, carbon dioxide fixation is performed by the enzyme ribulose-1,5-bisphosphate carboxylase oxygenase (RuBisCo) [26]. In many ways, RuBisCo is a remarkable enzyme, capable of fixing carbon dioxide despite the fact that atmospheric levels of this gas are only around 0.04 per cent. There currently exist no artificial catalysts capable of fixing carbon dioxide at such low concentrations at ambient temperature. Hence, the development of robust catalysts for both carbon dioxide fixation and reduction to fuels remains an enormous scientific and technological challenge. Perhaps the best place to start in such circumstances are those catalysts that are known to reduce CO_2 electrochemically, i.e. those catalysts that will reduce carbon dioxide given an appropriate electron input from an easily controlled source (the electrode in this case) [27]. Finding good electrocatalysts for CO_2 reduction in this 'isolated' approach need not be a drawback to their use in molecular artificial photosynthetic ensembles, provided these RuBisCo mimics can be compartmentalized effectively. Above all, it is this move to proper compartmentalization in molecular photosynthetic devices that Nature teaches us is essential, and which will allow discoveries across the chemical sciences to be integrated into workable artificial photosynthetic machines.

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