Prospects for conversion of solar energy into chemical fuels: the concept of a solar fuels industry

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There is, at present, no solar fuels industry anywhere in the world despite the well-publicized needs to replace our depleting stock of fossil fuels with renewable energy sources. Many obstacles have to be overcome in order to store sunlight in the form of chemical potential, and there are severe barriers to surmount in order to produce energy on a massive scale, at a modest price and in a convenient form. It is also essential to allow for the intermittent nature of sunlight, its diffusiveness and variability and to cope with the obvious need to use large surface areas for light collection. Nonetheless, we have no alternative but to devise viable strategies for storage of sunlight as biomass or chemical feedstock. Simple alternatives, such as solar heating, are attractive in terms of quick demonstrations but are not the answer. Photoelectrochemical devices might serve as the necessary machinery by which to generate electronic charge but the main problem is to couple these charges to the multi-electron catalysis needed to drive energy-storing chemical reactions. Several potential fuels (CO, H₂, HCOOH, NH₃, O₂, speciality organics, etc.) are possible, but the photochemical reduction of CO₂ deserves particular mention because of ever-growing concerns about overproduction of greenhouse gases. The prospects for achieving these reactions under ambient conditions are considered herein.

1. Background

As a rough approximation, our current energy consumption on a worldwide scale amounts to something like 15 trillion watts of power, of which about 85 per cent comes from combustion of fossil fuels such
as oil, coal and natural gas. This massive fossil fuel consumption leads to the inevitable production of unfortunate side-products that themselves present major problems, including climate change, acidified oceans and oil spills. There can be little doubt that these problems will grow in importance over the coming years, not least because of population growth and an escalation in our energy usage; the latter is expected to double before 2050 (as discussed by Lewis & Nocera [1]). Additional concerns can be raised about national security in terms of providing sustainable energy supplies. Indeed, Europe (and most of the individual countries) depends heavily on external supplies of energy and this situation is far from healthy. As a consequence, environmentally friendly fuel production has become a goal of major strategic importance across the globe at both national and international levels. The urgent, if not immediate, introduction of renewable energy sources presents serious challenges to contemporary science [2] but key steps have been taken already. To be successful and to maintain the need to cover critical scientific challenges, it is necessary to pursue a targeted, multidisciplinary approach that covers chemistry, physics, engineering and biology. We are at the beginning of this adventure and it is unclear whether sufficient funding will be made available to meet the scientific demands. It can only be hoped that lessons from the past, where the price of gasoline determined the level of support for artificial photosynthesis, will be put to good use.

Renewable power sources, especially in the guise of solar cells [3,4], tidal [5] and wind [6] turbines, are set to help replace fossil fuels, and there are streams of reports offering improved efficiencies and lower costs in terms of electricity production. This is important and needs to be further encouraged. The main problem with electricity, however, is that it is hard to store on a massive scale and, by itself, does little to offset escalation of CO₂ levels. As such, it cannot be relied upon for most heavy industry and transportation applications, such as ships, planes or agricultural vehicles. Many citizens worry about building new nuclear power stations. The answer in many researchers’ minds is to capture sunlight in the form of chemical potential [7] and to devise strategies for the production of a range of fuels that could fulfil the role as feedstocks. There are indications that this route is viable but there is no solar fuels industry at this moment. The choice of putative solar fuels is large, perhaps this is a detrimental point that loses focus, and there can be little doubt that we must explore all of these possibilities. Even so, there is an overwhelming necessity to demonstrate the scope of this (relatively) new field and to avoid overconfidence.

2. Objective

Of the potential renewable energy sources, solar energy is the most abundant and, if harvested efficiently, is capable of meeting global energy needs for the foreseeable future [1]. Most ongoing solar energy research is focused on direct conversion to electricity, by way of photovoltaic devices [8–10], or to high-temperature heat, via solar thermal procedures [11]. Cost-effectiveness and conversion efficiencies are of major importance but so too is storage. The latter is primarily in the form of low-cost batteries [12]. Additional research is directed towards the provision of small power units for application as personal energy supplies or for remote installations where cost is less important. We now direct attention to the main problem: the provision of massive supplies of energy by capture and storage of sunlight, allowing for the known difficulties associated with solar energy conversion in a non-intense (if not gloomy) environment as found in (say!) northern Europe.

3. Solar fuel

A fuel is any material which stores energy that can later be extracted to perform mechanical, electrical or chemical work in a controlled manner. Most fuels used by humans undergo a redox reaction in which a combustible substance releases energy after it ignites and reacts with the oxygen in the air. Other processes used to convert fuel into energy include various exothermic
chemical reactions and nuclear processes. Fuels are also used in cellular respiration, where organic molecules are oxidized to release usable energy. Hydrocarbons are by far the most common source of fuel. We can recognize the so-called biofuels, which can be broadly defined as solid, liquid or gas fuel consisting of, or derived from, biomass. Biomass can also be used directly for heating or power. A major advantage for biofuel relates to the fact that it can be produced from any carbon source that itself can be replenished rapidly. We are familiar with fossil fuels, primarily coal and petroleum (both liquid and gas), formed from the fossilized remains of ancient plants and animals over some hundreds of millions of years. Finally, we are aware of nuclear fuel, this being any material that is consumed to derive nuclear energy. There is, at present, no consensus as to what is meant by a solar fuel!

A solar fuel can be defined as ‘an energy-rich material generated from an abundant, cheap substance, such as water or CO₂, using sunlight as the only energy input’. In essence, the goal is to produce a CO₂ lean fuel from water, or readily available reagents produced as by-products from existing industrial processes, under illumination by sunlight. The product, to be classified as a fuel, must be storable. Some important compromise must be built into the approach from the beginning that deals with the lack of sunshine at certain times, stretching over extended periods in some densely populated locations. Above all, future funding for scientific research into this field demands that large-scale demonstration models are introduced sooner rather than later.

4. Identifying needs

The worldwide production of electricity in 2008 was 20 261 TWh (Statistical Review of World Energy 2009, BP), which represents something in the region of 11 per cent of the solar energy the Earth receives in 1 h (174 000 TWh). Sources of electricity were fossil fuels 67 per cent, renewable energy 18 per cent and nuclear power 13 per cent: the direct combustion of oil was only 5.5 per cent. Ninety-two per cent of renewable energy was hydroelectric, followed by wind at 6 per cent and geothermal at 1.8 per cent. Most scientists agree that fossil-fuel-based electricity generation accounts for a significant portion of world greenhouse gas emissions; in the USA, electricity generation accounts for nearly 40 per cent of emissions, whereas fossil fuel combustion for electric power generation is responsible for 65 per cent of all emissions of SO₂, a major contributor to acid rain, and other important pollutants such as NOₓ, CO and particulate matter. It is also important to recall that most large-scale thermoelectric power stations consume considerable amounts of water for cooling purposes and that this fact, by itself, is a cause for concern. A significant fraction of our total electricity production is used for industrial and domestic heating and/or cooling. It is clear that solar energy conversion could be invaluable in this area.

Again in reference to 2008, solar photovoltaic cells accounted for only 0.06 per cent of total electricity production, whereas solar thermal devices amounted for a mere 0.004 per cent. Unlike solar heat concentrators, photovoltaic panels convert sunlight directly to electricity. Although sunlight is free and abundant, solar electricity is still usually more expensive to produce than large-scale mechanically generated power owing to the cost of the panels. Low-efficiency silicon solar cells have been decreasing in cost and multi-junction cells with close to 30 per cent conversion efficiency are now commercially available. Over 40 per cent efficiency has been demonstrated in certain experimental systems. Until recently, photovoltaics were most commonly used in remote sites where there is no access to a commercial power grid, or as a supplemental electricity source for individual homes and businesses. Recent advances in manufacturing efficiency and photovoltaic technology, combined with subsidies driven by environmental concerns, have dramatically accelerated the deployment of solar panels.Installed capacity is growing by 40 per cent per year, led by increases in Germany, Japan, California and New Jersey.

Within the UK, we can make a crude breakdown of our energy needs (DECC report: Energy consumption in the UK) according to table 1. This shows that the two main areas for energy consumption are transport and domestic needs. This might be surprising in view of the widespread notion that the UK is a region of heavy industry. Nonetheless, it is clear that we could
Table 1. Breakdown of the main energy consumption modes for the UK.

<table>
<thead>
<tr>
<th>primary usage</th>
<th>percentage</th>
<th>domestic breakdown</th>
</tr>
</thead>
<tbody>
<tr>
<td>transport</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>industry&lt;sup&gt;a&lt;/sup&gt;</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>services</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>domestic</td>
<td>34</td>
<td></td>
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<tr>
<td>heating</td>
<td>57</td>
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<td>hot water</td>
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<td></td>
</tr>
<tr>
<td>appliances</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>cooking</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>lighting</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Includes what might be termed loosely as ‘commercial’.

5. Photochemical heat production

Alternative routes for using sunlight as a source of domestic heating have been considered. One interesting observation in this respect relates to the so-called South Andros Black Holes. Here, a dense 1 m thick layer of phototrophic purple-sulfur bacteria is present at a depth of approximately 18 m and gives rise to the characteristic colour. These bacteria function as a highly effective heat engine and maintain the temperature in the vicinity of the bacteria at a steady 36<sup>°</sup>C. This is a remarkable achievement but one that we might conceivably duplicate at an artificial level [13]. In fact, there is no difficulty in devising photochemical cycles capable of converting photonic energy into (low-temperature) heat by way of non-radiative channels. The problem is to generate high-temperature heat and to store the energy in such a manner that the desired heat can be released as and when needed. This is quite different to simply depositing the heat into the local environment immediately after excitation.

This situation was considered first some 30 years ago, and several putative cycles were identified. One of the best photochemical storage systems is the interconversion between norbornadiene and quadricyclane [14]. This type of photoisomerization is particularly clean and essentially independent of temperature. Although near-UV light is required to drive the isomerization of norbornadiene, it is possible to promote the reaction using triplet state sensitizers [15] that absorb in the visible region. The isomerization step can store appreciable amounts of energy that can be converted to heat by passing the quadricyclane product over a transition metal catalyst (figure 1). The main drawbacks are poor light-harvesting capabilities, the need to use organic solvents and poor catalytic properties of the recycling agent. Nonetheless, this is a valuable practical application of solar energy conversion.

It is worth considering if new forms of photoisomer-based cycles could be found that operate in aqueous solution. Ideally, this would involve a photochemical adenosine triphosphate (ATP) synthesis driven by visible light. In itself, this is a major challenge but it is not unrealistic. As a simpler alternative, it is conceivable to design photochemical cycles around the interconversion of nicotinamide adenine dinucleotide (NAD<sup>+</sup>) and its reduced form (NADH), although it is necessary to avoid dimerization of the intermediary NAD· radical. This cycle can be driven enzymatically using photonic energy as the input but this process is usually achieved [16] at the expense of consuming an added sacrificial organic substrate, such as triethanolamine. It is

make an important contribution to our global energy picture by replacing fossil fuels used in domestic uptake with solar fuels. Looking at the breakdown of UK domestic energy consumption, we can identify heating as being the biggest single factor. This is critical information for defining our priorities for the type of solar fuels we might consider.
more difficult to design tandem photosystems that combine oxidation of NADH (or reduction of NAD\(^+\)) with a non-sacrificial reaction. In part, this problem is acerbated by the imbalance of protons: for example, reduction of NAD\(^+\) can be considered as a hydride transfer reaction, whereas \(\text{O}_2\) evolution from water leads to the accumulation of four protons. Nonetheless, these cycles are important as a means by which to overcome the problems associated with collection and storage of the fuel. It is highly likely that further attention will be given to such systems, especially artificial ATP synthesis, in the near future.

6. Photochemical synthesis

Photochemistry can be used as a tool to synthesize valuable materials, including novel pharmaceuticals. It is often proposed that sunlight could be used profitably to generate industrial-scale quantities of key starting compounds, such as epoxides. Within reason, this can be achieved by sensitized formation of singlet molecular oxygen and its subsequent reaction with an alkene. There are, however, problems of selectivity and specificity with regards to singlet molecular oxygen attack on organic compounds. Could the oxygen be derived from water? Well, this possibility has been considered but the outcome is not too promising.

An alternative approach is to use a waste organic substrate as a sacrificial agent by which to generate a valuable fuel using photochemical methods [17]. Such a strategy is often used to isolate one half of a redox cycle so as to optimize a particular catalytic cycle (e.g. \(\text{H}_2\) generation) but leads to serious problems at a later stage. We can raise the question here as to whether there exists a suitable dump of waste product that could be upgraded by way of a photochemical reaction that generates a viable fuel. On a slightly different tack, a similar reaction could be used to remove an important pollutant that accompanies an industrial process. One substrate that springs to mind is glycerol, a by-product of biodiesel production [18]. Although glycerol is a useful ingredient in cosmetic products, there is a large surplus to such an extent that it is now burned at high temperature in order to keep stocks at a reasonable level. Because it contains easily removable hydrogen atoms, glycerol can be used as a substrate for \(\text{H}_2\) generation using a simple benzophenone derivative as sensitizer [19] under near-UV illumination (figure 2). Indeed, illumination of the water-soluble benzophenone derivative in aqueous solution containing glycerol at concentrations above a few per cent by volume and a suitable reduction catalyst (e.g. colloidal Pt) leads to \(\text{H}_2\) generation. Most of the hydrogen atoms can be extracted from glycerol in this manner and converted into collectable \(\text{H}_2\). Such benzophenone-based sensitizers are non-toxic, being used as UV initiators for dental fillings and activators for emulsion paint, and cheap. Of course, they are destroyed during the process, but the overall reaction is autocatalytic because other carbonyl compounds are generated during the free-radical cycle. Furthermore, the final carbon-based residue can be suitably downgraded as a non-toxic reagent or converted to a crude fertilizer by adding ammonia to the initial reaction mixture, which becomes fixed into the carbon backbone. Other waste substrates, such as aqueous ethanol or biomass, can be considered along these lines and used as substrates for \(\text{H}_2\) formation.
Looking back over the myriad of artificial photosynthetic systems published during the late 1970s and early 1980s, one particular system stands out as being especially relevant to the present discussion [20]. This photosystem uses a complex mixture of bioinspired ideas to decompose ethanol into acetaldehyde and H$_2$ in water under ambient conditions (figure 3). The key component is a water-soluble tin(IV) porphyrin (SnP), which acts as a replacement for chlorophyll, that is easily reduced to the corresponding $\pi$-radical anion. Unlike most metalloporphyrins [21], the $\pi$-radical anion formed from SnP is stable in aqueous solution and resistant towards disproportionation; this is a critical point in terms of overall stability of the system. Under illumination, SnP is reduced by added NADH but the resultant $\pi$-radical anion reduces methyl viologen (MV$^{2+}$) to give the stable mono-cation radical that itself reduces water to H$_2$ on the surface of a colloidal Pt catalyst. This strategy leaves behind the oxidized form of NADH, namely NAD, but this latter species reacts with ethanol in the presence of alcohol dehydrogenase (ADH) to give the protons necessary for H$_2$ evolution. There is no change in pH and the system operates over prolonged illumination periods, in part because breakdown products from SnP (i.e. phlorin- and chlorin-type compounds) also function as sensitizers for the photochemical cycle. The overall quantum efficiency for H$_2$ production at pH 7 is 55 per cent, and a considerable fraction of the solar spectrum is harvested. Furthermore, the system uses only 1 per cent by volume ethanol in water and, as such, could be applied to extract the residual ethanol from biofuel production after the distillation step.

7. Photochemical water splitting

The ideal methodology for solar fuel production is based on the photochemical dissociation of water under ambient conditions. This is a non-trivial operation, made particularly difficult by
the need to transfer multiple electrons. There is also a problem of inconsistency in as much as H\textsubscript{2} formation is easiest in acidic solution but O\textsubscript{2} generation occurs better at alkaline pH. The energy requirement for water splitting is high because of the need to overcome substantial over-potentials associated with the individual electrochemical reactions. Indeed, as a crude approximation, the dissociation of one gallon of water requires an input of about 25 kWh. A further problem related to photochemical water splitting is that there are several important intermediates that can enter into side-reactions and thereby serve to lower overall efficiencies. This latter problem requires that electrons and/or positive holes are injected into the catalytic sites at a high rate in order to push the cycle through to the final product. The main problem here is associated with O\textsubscript{2} evolution.

At this point, it is important to stress that the application of sacrificial redox reagents, such as persulfate ions or triethanolamine, must be avoided. Traditionally [17], these reagents have been used to isolate either H\textsubscript{2} or O\textsubscript{2} evolution. They work extremely well but hide the fact that the intermediary radicals play critical roles in the subsequent chemistry—this point is often overlooked in the enthusiasm to report H\textsubscript{2} or O\textsubscript{2} yields. Replacing the sacrificial reagent with a reversible redox couple causes a massive fall in reaction efficiency, or stops the reaction entirely. There are, indeed, few cases of O\textsubscript{2} evolution from water where a reversible redox shuttle is involved. The most successful of these processes uses Fe\textsuperscript{2+}/Fe\textsuperscript{3+} as the redox couple [22] and allows O\textsubscript{2} evolution to proceed in acidic solution with modest quantum yield (figure 4). Although it has long been argued that sacrificial reagents help to optimize the catalytic performance, this is not really the case. Of the many thousands of examples where sacrificial redox reagents have been used to isolate the required catalytic step, only a small handful have been successfully carried through to the next stage.

Regarding the photonic input, there seems no alternative but to rely on a semiconductor as the actual light collection unit, perhaps used in consolidation with an organic-based solar concentrator. The latter ensures an adequate supply of photons/electrons to the catalytic site. It seems appropriate to go one stage further and insist on coupling together two such units, rather than rely on a single unit with or without the ancillary solar concentrator. The main advantage of tandem units is that their individual properties can be tailored for particular purposes. Continuing along this line, it can be argued that water splitting can only be realized by way of two coupled photo-electrochemical steps, each performed at a specific electrode. Such a system is an upgrade of the original Fujishima–Honda photo-assisted electrolysis of water—this remains one of the most important observations in the field [7]. A prototype of this design was described recently by Mallouk and co-workers [23,24] and serves as a useful starting point for future discussion. It might also be mentioned that a molecular-based photo-electrochemical system was introduced [25] recently whereby prior reduction of an appended electron acceptor was used as a means by which to amplify the reduction potential of a nearby excited state. This system, being the first of its kind, functions as a crude harmonic generator to increase redox power (figure 5) and could have important applications for light-driven energy storage.

Regardless of the exact nature of the solar fuel, it is essential that any large-scale operation evolves O\textsubscript{2} from water during the photochemical cycle [26]. This reaction involves the transfer of four electrons and liberates four protons; consequently, the pH will decrease during illumination, thereby changing the chemical potential, unless there is a complementary light-driven process.
Figure 5. Scheme used for the photo-assisted electrolysis of a substrate (S) by a zinc porphyrin (ZnP) covalently attached to a polyoxometallate (POM). The approach requires prior reduction of the POM at an electrode surface. Illumination at ZnP causes a charge-shift reaction (csr) to occur and so generate a strongly reducing form of ZnP.

Table 2. Comparison of the observed rates and quantum efficiencies of $O_2$ evolution observed for various metal oxide catalysts under photochemical conditions.

<table>
<thead>
<tr>
<th>oxide</th>
<th>relative rate of $O_2$ evolution</th>
<th>quantum efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrO$_2$</td>
<td>27.0</td>
<td>61</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>25.5</td>
<td>58</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>18.6</td>
<td>42</td>
</tr>
<tr>
<td>Rh$_2$O$_3$</td>
<td>15.6</td>
<td>35</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>15.3</td>
<td>35</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>14.1</td>
<td>32</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>13.4</td>
<td>30</td>
</tr>
<tr>
<td>MgO</td>
<td>3.2</td>
<td>7</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>2.9</td>
<td>6</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>1.9</td>
<td>4</td>
</tr>
<tr>
<td>CdO</td>
<td>1.8</td>
<td>4</td>
</tr>
<tr>
<td>NiO</td>
<td>1.2</td>
<td>3</td>
</tr>
<tr>
<td>Fe$_5$O$_3$</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Obtained from Ventron.
$^b$ Obtained from Alpha.

that uses these protons at the same rate. Several metal oxides are known to function as good anodes for $O_2$ evolution and a critical comparison of such materials has been made under photochemical conditions [27]. The main results of this latter study are compiled in table 2. Unfortunately, most of the effective materials are based on very expensive and rare elements, although Co$_3$O$_4$ stands out as being a useful alternative. Despite its involvement in natural oxygen evolution, MnO$_2$ is a relatively poor catalyst for water oxidation under these conditions. This study does not address the mechanism of water oxidation, which might differ according to the type of oxide used as catalyst, but makes clear recommendations as to which materials are likely to work under illumination in any prototypic photo-electrochemical system. As such, we can identify IrO$_2$, RuO$_2$, Co$_3$O$_4$ and (to a lesser extent!) Rh$_2$O$_3$ and MnO$_2$ as being suitable materials for the anode. It is important to note that these experiments were made at pH 5, rather than in alkaline solution where $O_2$ evolution is more favoured thermodynamically. Other work with similar RuO$_2$- and IrO$_2$-based colloidal catalysts has stressed the importance of pH in terms of reaction kinetics and, in particular, the over-potential needed for water oxidation [28–31]. The need for a wide pH profile stems from the requirement to couple $O_2$ evolution with fuel formation.
and (iv) the generation of \( \text{O}_2 \) at low over-potential at neutral \( \text{pH} \), atmospheric pressure and aqueous solution, (ii) a potential route for self-repair, (iii) a carrier for protons in neutral water, natural photosynthesis, including (i) its formation from cobalt(II) phosphate. Thus, the cathode developed therein exhibits many elements of multiple redox states \[33\]. The situation with cobalt catalysts is much improved, and recent considerable research has been expended on designing manganese porphyrins able to sample +2 oxidation states. At present, it is beyond our capabilities to prepare an artificial analogue based on manganese, although +3 oxidation states. At present, it is beyond our capabilities to prepare an artificial analogue based on manganese, although

<table>
<thead>
<tr>
<th>Oxide</th>
<th>( x )</th>
<th>( T (\degree \text{C}) )</th>
<th>Relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PtO}_2 )</td>
<td>1.05</td>
<td>—</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>260</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>400</td>
<td>1.1</td>
</tr>
<tr>
<td>( \text{IrO}_2 )</td>
<td>2.08</td>
<td>—</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>400</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>500</td>
<td>27.3</td>
</tr>
<tr>
<td>( \text{MnO}_2 )</td>
<td>0.67</td>
<td>—</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>200</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>300</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>400</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>650</td>
<td>13.4</td>
</tr>
<tr>
<td>( \text{Rh}_2\text{O}_3 )</td>
<td>3.10</td>
<td>—</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>200</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>550</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Table 3. Rates of \( \text{O}_2 \) evolution using various metal oxide hydrates (\( x \text{H}_2\text{O} \)) as catalysts and the effect of heating the hydrate for 2 hours in air at a particular temperature.

Of course, it is important to consider the physical state of the catalyst before reaching critical conclusions about which materials should be used in a large-scale practical system. Similar studies were carried out to assess the ability of hydrous metal oxides to function as good \( \text{O}_2 \) evolving catalysts under photochemical conditions. Again, it was found \[27\] that \( \text{IrO}_2 \cdot \text{nH}_2\text{O} \) forms the most effective catalytic centres at \( \text{pH} \) 5, with \( \text{RuO}_2 \cdot \text{nH}_2\text{O} \) and \( \text{MnO}_2 \cdot \text{nH}_2\text{O} \) being less effective but still viable candidates for the anode (table 3). A point of interest with colloidal \( \text{IrO}_2 \cdot \text{nH}_2\text{O} \) is that the material possesses a clear blue colour, presumably due to intervalence charge-transfer transitions, that should favour detailed mechanistic investigations. Indeed, some preliminary work has been performed \[30,31\] under pulse radiolytic conditions to monitor the dynamics of hole injection into the colloid. It was found that the rate of the initial hole injection was sensitive to \( \text{pH} \) but always remained slow. Clearly, this step is going to be one of the rate-limiting issues in water oxidation, even allowing for the slow provision of holes at the catalytic site.

The natural water oxidation catalyst found \[32\] in green plants is based on a tetrameric manganese cubane structure that shuttles between the +2 and +3 oxidation states. At present, it is beyond our capabilities to prepare an artificial analogue based on manganese, although considerable research has been expended on designing manganese porphyrins able to sample multiple redox states \[33\]. The situation with cobalt catalysts is much improved, and recent results indicate that an effective electrochemical catalyst for water oxidation can be engineered \[34\] from cobalt(II) phosphate. Thus, the cathode developed therein exhibits many elements of natural photosynthesis, including (i) its \textit{in situ} formation from Earth-abundant metal ions in aqueous solution, (ii) a potential route for self-repair, (iii) a carrier for protons in neutral water, and (iv) the generation of \( \text{O}_2 \) at low over-potential at neutral \( \text{pH} \), atmospheric pressure and room temperature. Furthermore, the new material has been interfaced \[35\] with light-harvesting semiconductors so as to develop devices capable of the solar-to-fuels conversion at an overall efficiency of 4.7 per cent for a wired configuration and 2.5 per cent for a wireless configuration when illuminated with 1 sun (100 mW cm\(^{-2}\)) of air mass 1.5 simulated sunlight. These cells consist of a triple junction, amorphous silicon photovoltaic interfaced to a NiMoZn \( \text{H}_2 \)-evolving catalyst and the above-mentioned oxygen-evolving catalyst (figure 6). The devices described here
are able to realize the desired solar-driven water-splitting reaction at reasonable efficiency and hold considerable promise for the future, provided the systems can be increased in scale from laboratory demonstration models to practical entities.

Fujishima and Honda reported [7] the first example of the UV photo-assisted electrolysis of water using a platinized TiO\textsubscript{2} electrode in 1972 and more efficient multi-junction photoelectrodes have been developed subsequently [36–38]. More recently, Mallouk and co-workers reported a system (figure 7) that uses visible light to split water into hydrogen and oxygen assisted by a small applied voltage [23]. Their system uses the above IrO\textsubscript{2}·\textit{n}H\textsubscript{2}O cluster as the water oxidation catalyst, together with a Pt cathode. The photochemical reaction centre comprises a TiO\textsubscript{2} film impregnated with a ruthenium(II) poly(pyridine) complex as sensitizer. The system is a hybrid between the Fujishima–Honda cell and the well-known Grätzel-type dye-injection solar cell. The low quantum efficiency of approximately 1 per cent is due to slow hole injection into the IrO\textsubscript{2}·\textit{n}H\textsubscript{2}O nanoparticles from the oxidized dye. This reaction does not compete effectively with back electron transfer from TiO\textsubscript{2} to the dye. However, further tuning is possible [24] and a viable prototype looks likely to emerge in the near future.

Catalysts for the reduction of water to H\textsubscript{2} have been available for many decades [39], although most are based on expensive and rare metals such as Pt, Ru or Ir. These materials require small over-potentials but are not selective and tend to catalyse hydrogenation of any unsaturated organic matter present in the system. Suitable photocathodes for water reduction can be fabricated from stabilized Cu\textsubscript{2}O, and this p-type semiconductor is a promising material for the photo-assisted electrolysis of water [40]. A critical operating problem in this domain relates to the simultaneous presence of H\textsubscript{2} and O\textsubscript{2}. This situation makes separation of the gases a difficult
task and, because a catalyst is usually in the close vicinity, results in recombination reactions (i.e. a Groves type fuel cell). Molecular oxygen competes with protons for the solar-generated reducing equivalents and leads to corrosion of the materials. The search for highly effective catalysts that display excellent specificity for H₂ evolution has included certain enzymes [41] that can be adhered to semiconductor electrodes. The enzymes can demonstrate high turnover numbers and good selectivity but most are poisoned by the presence of molecular oxygen. Recent research, however, has identified [42] certain hydrogenase strains able to tolerate a low pressure of O₂.

The competing chemistry introduced by the presence of O₂, together with the difficulty associated with the collection of H₂ over a widespread area, has helped direct research towards other targets. Most notable among these is the photochemical reduction of O₂ to hydrogen peroxide. The latter is a useful product provided it is generated at concentrations in excess of approximately 10 per cent by volume. Again, there are problems to identify selective catalysts, although Au nanoparticles look promising in this field. It is necessary to avoid the simultaneous presence of H₂ and H₂O₂ because of catalysed chemical reactions, but rapid progress seems highly likely in the very near future. As with H₂ liberation, enzyme catalysts are available to promote the key reduction step.

8. Carbon dioxide reduction

Solar-based production of organic chemicals by the reduction of CO₂ is an increasingly important area that addresses global warming and fossil fuel shortages. A major advantage of this route is that CO₂ can be converted to other energy-storing chemicals such as syngas, formic acid, methane, ethylene, methanol and dimethyl ether: an excellent review of the available directions for CO₂ reduction has appeared recently [43]. In developing a viable strategy along this direction, it must be accepted that water is the sole reagent to be considered as the source of both electrons and protons. There are, in fact, many metal complexes able to reduce CO₂ with low quantum efficiency under illumination in the presence of sacrificial reagents. Usually, these systems operate in anhydrous organic media, typically N,N-dimethylformamide, saturated with high concentrations of CO₂. These conditions are not conducive to setting up a solar fuels industry! On the other hand, natural photosynthesis does a fine job of the photochemical fixation of CO₂ to carbohydrates under ambient conditions. This realization has led to the installation of large-scale facilities using microalgae to extract CO₂ from effluent gases produced by essential industrial processes. Most notable in this area is the Secil process operating in Portugal that uses CO₂ from cement manufacture as a feedstock for biomass production (see http://www.secil.pt/default_en.asp).

Major problems associated with the photochemical reduction of CO₂, which is clearly the best way forward in terms of environmental protection, stem from the high over-potentials associated with most electrodes, poor selectivity because of competing H₂ formation or O₂ reduction, and low concentration of CO₂ in the atmosphere. Nonetheless, certain semiconductors are known to display photocatalytic activity towards CO₂ reduction in water, albeit with low quantum efficiencies. A recent breakthrough [44] in this field has seen the introduction of a tandem arrangement that couples an InP photocathode for CO₂ reduction in water with a TiO₂ photoanode for H₂O oxidation (figure 8). Selectivity for the reduction of CO₂ to formate is provided by coating the zinc-doped indium phosphide p-type photocathode with a ruthenium-based polymer, [Ru(4,40-di(1H-pyrrolyl-3-propyl carbonate)-2,20-bipyridine)(CO)₂], as the electrocatalyst. The efficiency for converting sunlight into chemical energy is only around 0.04 per cent but this is a promising start.

While many attempts at the two-electron photoreduction of CO₂ to CO or formic acid have been described in the literature, little success has been achieved in regards to the six-electron reduction of CO₂ to methanol. The complete reduction of CO₂ to CH₄ using water vapour as the source of hydrogen has been observed with wide-band-gap semiconductors such as TiO₂ [45] or zinc orthogermanate (Zn₂GeO₄) nanostructures [46]. The latter material, which has a band gap of 4.5 eV, is a poor sensitizer for CH₄ production but, in line with earlier reports concerning
Figure 8. Tandem (or Z-scheme) photo-electrochemical approach used to reduce CO₂ to formate in aqueous solution. The photoanode comprises band gap excitation of platinized TiO₂, whereas the photocathode is a Zn-doped InP electrode coated with a polymeric ruthenium(II) complex. (Online version in colour.)

Ammonia is essential for life, because it provides the nitrogen needed for building proteins and DNA, and because of its critical role as a fertilizer. It is considered that in excess of almost one billion tonnes of ammonia are formed each year via reduction of atmospheric nitrogen by nitrogenase enzymes. About the same amount is produced abiotically through the Haber–Bosch reaction, which is arguably the single most significant industrial process ever discovered. This artificial route to NH₃ is energy intensive but necessary to sustain agriculture and human development. It is natural to consider developing photochemical routes to N₂ fixation that might circumvent the Haber–Bosch process, possibly by incorporating some aspects of nitrogenases in the chemistry. Discovering an effective catalyst for the mild generation of NH₃, either by direct reduction of N₂ or its combination with H₂, would be a tremendous advance over current technology and, by itself, could ensure stable future funding for artificial photosynthesis. Of course, this chemistry is exceedingly difficult.

It is generally considered that the abiotic fixation of N₂ requires a Mo-based catalyst. Indeed, few catalytic cycles are known that will reduce N₂ to NH₃ under ambient conditions [49]. In one case, a single Mo(III) centre serves as catalyst [50], whereas a second system yields hydrazine as the primary product, which disproportionates into nitrogen and ammonia [51]. Quite separately, the radiolytic and UV-photochemical reduction of N₂ to NH₃ has been realized in aqueous
solution using colloidal metal particles as catalyst [52]. In this case, the catalysts were far from selective for N₂ reduction, with H₂ evolution occurring in acidic solution, whereas the overall efficacy of the process was found to depend on the type of reducing radical. Nonetheless, this pioneering work provides encouragement for further exploratory research in this important area.

10. Conclusions and prospects

The supply of secure, clean, sustainable energy is a major scientific and technological challenge that must be solved within the next few decades in order to avoid catastrophic changes in society. There are related issues for national and economic security and environmental control that are likely to raise our urgency for seeking genuine solutions to the renewable energy problem. To overcome the technical problems associated with the development of a national solar fuels industry demands the identification of new protocols for the photochemical production of carbon-based fuels and for the recovery of CO₂ from the atmosphere. The conversion of sunlight into chemical potential is based on the capture and conversion of solar energy, the liberation of molecular oxygen from water and the subsequent collection and storage of the fuel. In addition to concerns about cost-effectiveness of this basic strategy, it is necessary to accept that, relative to fossil fuel-derived energy, solar energy is diffuse and seasonal, at least in northern Europe. As such, materials costs must be kept very low and long-term storage is essential if we are to succeed in establishing a viable solar fuels industry on these shores.

Molecular-based artificial photosynthetic models have played important roles in the historical development of the field. There have been some hugely imaginative attempts to construct molecular analogues of both the natural light-harvesting antennae and the bacterial reaction centre complex. Although numerous photosystems have been set up that evolve H₂ or O₂ under illumination, there seems little likelihood that such approaches can be made practical. The same situation holds for reduction of atmospheric CO₂ in the presence of molecular oxygen. By contrast, the photochemical dehydrogenation of waste materials is both viable and economical, provided adequate stocks of the waste compound are available and that the entire process is carried out locally. Equally promising is the development of practical outlets for light-induced heat storage. There can be little doubt that commercial outlets could be found along this route and that domestic heating could be delivered by such bioinspired strategies. The only remaining requisite here is to develop water-based systems using small molecular fragments such as ATP analogues.

Large-scale solar capture and conversion can be accomplished by making use of photovoltaic devices. The primary challenge here is to increase the cost-effectiveness for delivered solar electricity. Do we have sufficient sunlight in the UK to drive such technology? If not, is it possible to harvest solar energy from the desert and transport the generated electricity several thousands of miles to the UK? These are major issues but, in terms of solar fuel production, change nothing: there is still the critical need to develop effective and selective catalysts capable of water oxidation and fuel generation under ambient conditions. Other reports will focus attention on the cost of solar electricity but we have to recognize that storage is best achieved by way of fuel generation. The latter requires water oxidation to O₂ at minimum over-potential and on a huge scale. What about the fuel?

The storage of sustainable energy in the form of chemical fuels (e.g. hydrocarbons and alcohols) by means of artificial photosynthesis using CO₂ and H₂O should enable a CO₂ neutral power generation infrastructure close to our present commitment to fossil fuels. This would require minimum disruption of our current machinery but demands the identification of selective and ultra-efficient catalysts. The on-site collection of gases over a wide area is problematical, as is the prior removal of O₂ from the cell housing the cathode. In this respect, the conversion of O₂ to HOOH looks to be the easiest option. The corresponding conversion of CO₂ to HCOOH is more attractive, in many respects, but an order of magnitude more difficult to achieve. In terms of setting up a large-scale demonstration of solar fuel production, we could do worse that develop a robust protocol for local production of hydrogen peroxide. On a longer-term basis, the route
to methanol production from CO₂, no doubt this is a hazardous journey, has been opened by the concept of involving a pyridinium-based relay and this could be our most realistic target. Mimicking the role of the FeMo nitrogenases in N₂ fixation might be a step too far at the moment but fundamental research in this area is needed desperately. A high fraction of worldwide energy supplies is diverted to the fixation of N₂, a process that by itself is responsible for massive population growth, using established chemistry at high temperatures and pressures. The selective reduction of N₂, probably the most stable diatomic molecule, to NH₃ by protons and electrons at room temperature and atmospheric pressure remains a challenge for future generations.

We thank Newcastle University for providing facilities useful for the compilation of this article. Part of the fundamental research underpinning this discussion was supported by EPSRC.

References


