Interfacial Photoelectrochemical Synthesis of Organic Molecules: Solar-Induced Electrochemical Organic Transformations

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Abstract

Many oxidation and reduction reactions in conventional organic synthesis rely on harsh conditions, toxic or corrosive substances, and environmentally damaging chemicals. In addition, competing reactions may take place, some of which produce hazardous waste products, and therefore reaction selectivity suffers. To overcome such synthetic drawbacks, an enormous effort is being devoted to find alternative processes that operate much more efficiently, requiring milder conditions to contribute to a more green economy and provide urgently needed new pathways with enhanced selectivity. Fortunately, there is a strategy that has attracted global interest from multiple disciplines that involves the use of sunlight to perform artificial photosynthesis, in which a photoelectrochemical (PEC) cell splits water into hydrogen fuel, reduces CO_2 into hydrocarbons and other "solar" fuels, and more recently, convert organic chemicals into higher value products. Lately, photoanode and photocathode materials have emerged as useful to perform organic oxidations and reductions for the chemical synthesis of important molecules, other than just hydrogen or oxygen. However, the vast majority of previously reported work focuses on degradation of unwanted and dangerous chemicals, whereas solar-induced organic transformations have attracted much less attention. In the present paper, we outline some of latest research efforts in using photoelectrochemical cells to facilitate organic oxidation and reduction reactions for valuable substances avoiding toxic reagents and expensive precious metal catalysts. We also consider future developments that will enable such a technology to broaden its scope.

Introduction

Since the discovery of the photoelectric effect, researchers have been attracted to the idea of transforming plenteous solar light into electrical energy by means of photovoltaics and solar fuel generation with photoelectrochemical (PEC) cells (**Fig 1**).[1] PEC cells have been comprehensively studied and subsequently applied to the splitting of water, the reduction of carbon dioxide into solar fuels, as well as the production of C1- C2 chemicals and hydrogen peroxide.[2–4] A PEC device is designed to perform two operations: the first is to employ the photovoltaic effect in order to produce electrical energy from visible light and the second is to facilitate efficient photoelectrolysis. Typically, a semiconducting photoelectrode immersed in an electrolyte is exposed to solar light, which generates electron-hole pairs that are used to drive a redox reaction.[5] In a simple PEC cell, the other electrode is a conventional metal electrode, but the photovoltage generated in such systems is generally too low to facilitate water spltting.. Tandem PEC cells, on the other hand, generate higher photovoltages since they consist of a photoanode (n-type) material where photogenerated holes induce oxidation and a photocathode (p-type) material that causes reduction via photogenerated electrons.[6]. By contrast with water oxidation, oxidation of organic substrates is generally more facile and therefore the photovoltage required is lower. The kinetics of light-driven water splitting for the generation of hydrogen are sluggish because the oxygen evolution reaction (OER) is a four-electron transfer process. Electrolysers rely on expensive metal catalysts such as iridium, alternative high-performance materials are much sought after.[7] From an organic chemistry perspective it is possible to apply the PEC principle to generate organic compounds such as fuels as well as transform other organic molecules into others that have a higher value in a green and sustainable manner using a lower photovoltage than that required for water splitting. [8,9] There is an also an advantage of using an organic reaction medium (electrolyte) for organic transformations such as acetonitrile (MeCN) which reduces photocorroison of electrode. At present, however, only a few reactions have been explored.
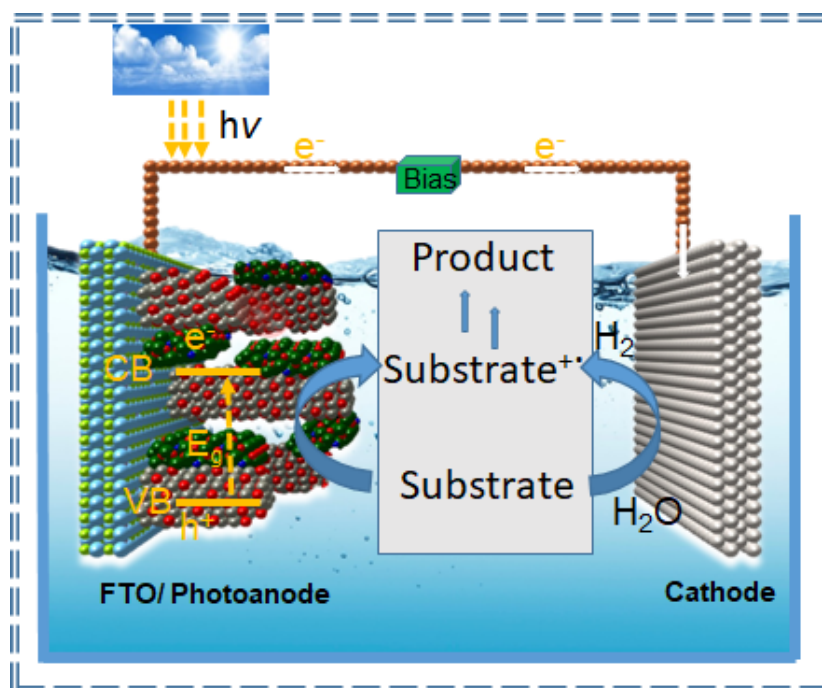
Fig 1. *Photoelectrochemical cells for solar-induced organic transformations.*

A study of the current literature reveals that so far only a few photoelectrode materials have been tested in organic PEC transformation systems, but there are many more with the potential to join this group. In this report, our focus is to understand the applicability of PEC systems in organic synthesis fad to assess their future promise for organic chemistry. We believe that PEC cells have the potential to enable a wide range of oxidation and reduction reaction in organic synthesis in a way that will lead to safer, more selective and cost-effective chemical processes that are environmentally benign.

Interfacial Photoelectrochemical Organic Transformations:

Cha *et al.* reported the first example of PEC waste valorisation for biomass conversion into desired chemicals by oxidising 5-hydroxymethylfurfural (HMF) into 2, 5-furandicarboxylic acid (FDCA) using a $BiVO_4$ photoanode, 0.5 M borate buffer solution (pH 9.2) as the electrolyte and TEMPO as the redox mediator, all under AM 1.5G light irradiation.[10] HMF, derived from C6 monosaccharides, is regarded as an important intermediate for industrially relevant biomass conversions, while FDCA is a valued monomer for the fabrication of numerous polymers. Photooxidation of HMF was achieved with 93% Faradaic efficiency and a yield of ≥ 99%. Compared to the water oxidation, the onset potential for TEMPO oxidation was negatively shifted (**Figure 2a**) by *ca.* 0.7 V to 0.32 V versus RHE (corresponding to almost 700 mV less potential needed to oxidise HMF), indicating that the TEMPO oxidation is more favourable. The setup of this PEC system is shown in **Figure 2b**; holes in n-type $BiVO_4$ are photoexcited to the valence band, where they participate in the oxidation of TEMPO, which then drives oxidation of HMF to FDCA. Photoexcited electrons are transferred to a Pt electrode to reduce protons into hydrogen.
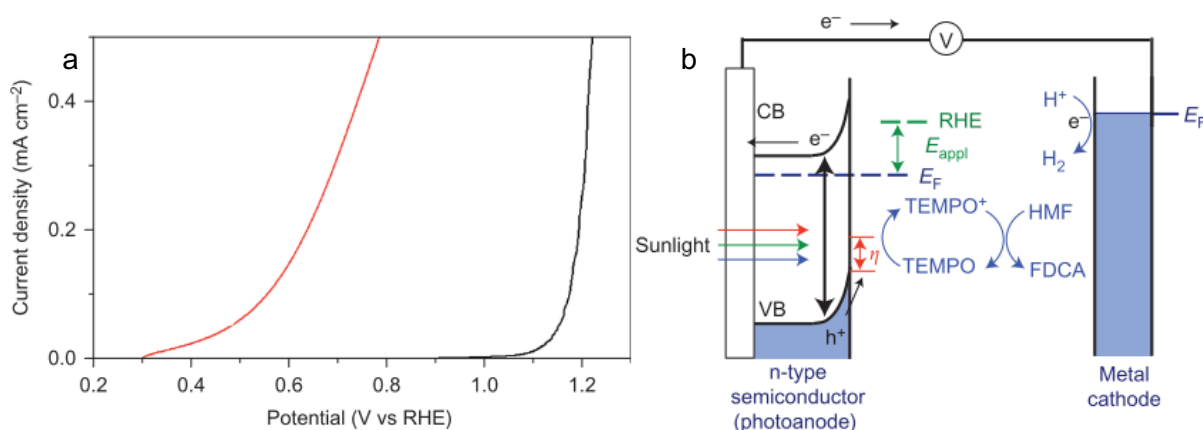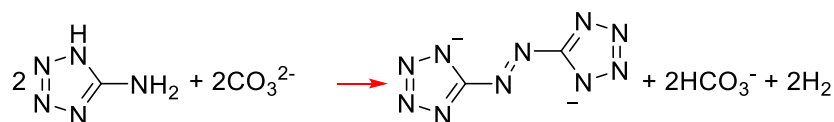
Fig 2. *a) Linear sweep voltammograms (LSVs) of a BiVO₄ photoande under AM 1.5G light (red line) and a Au electrode in the dark (black line); 0.5 M borate buffer solution (pH 9.2) containing 5 mM HMF and 7.5 mM TEMPO, with a scan rate of 10 mV s⁻¹. b) Proposed PEC mechanism for the TEMPO-mediated HMF oxidation. Reproduced from ref [10].*

In another work, the selective oxidation of HMF mediated by TEMPO was performed over BiVO₄ modified with a cobalt phosphate (CoPi) overlayer, to afford FDCA in 88% yield. The reaction was run for 2.7 h under AM 1.5G light with a sodium borate electrolyte (pH 9.2) at 0.64 V vs. RHE.[11] Transient photocurrent measurements reveal that a major improvement of efficiency can be attributed to the back reduction of oxidised TEMPO being inhibited by CoPi, reducing recombination losses. Interestingly, no oxygen was detected, revealing that the photoelectrochemical OER was completely suppressed, and thus illustrating the greater selectivity towards the TEMPO oxidation when comparing to BiVO₄ alone.[11] Furthermore, the OER activity was reported to be dependent on the CoPi electrodeposition time, with short times (i.e. 1 min) reducing the onset potential and increasing OER photocurrent, and longer times (i.e. 30 min) preventing the OER. A 30 min deposition time, producing CoPi layers with sufficient thickness, was also able to reduce the potential required for TEMPO oxidation by ~0.5 V, in addition to increasing the charge injection efficiency by a factor of seven (compared to lone BiVO₄) and thus, greatly improve the TEMPO oxidation photocurrent; no Faradaic efficiency loss to the OER was observed for the TEMPO oxidation with the Bi-Co (30 min) composite.

Nitrogen-rich heterocyclic 5,5'-azotetrazolate salts are used in industry and the military, in a range of applications such as fireworks, propellants, gas generators and ammunitions.[12,13] As an example, sodium 5,5'-azotetrazolate (SZT), a precursor to guanidinium salts of 5,5'-azotetrazolate, has been synthesised by the room temperature coupling reaction of 5-amino-1H-tetrazole (5AT) in 2M Na₂CO₃, under light irradiation using 2% W, 6% Mo co-doped BiVO₄ as the photoanode (**Scheme 1**).[13] The reaction, initiated by photogenerated holes, proceeded with a Faradaic efficiency of 80% at 1.2 V vs. RHE on the doped BiVO₄, which retained good stability during the 8 h reaction. The standard emf ($E^{\ominus}$) of the coupling reaction was calculated to be 0.37 V vs. RHE, indicating that it is more thermodynamically more facile than water splitting, as was observed through a higher photocurrent, and furthermore, oxidation was attributed to occur predominantly through holes rather than through possible H₂O₂ intermediates (from the water splitting). The reaction was occurred to a lesser extent over undoped BiVO₄, but did not proceed in the absence of visible light.

$$2\ \underset{\underset{N}{\overset{N}{\parallel}}}{\overset{\overset{H}{\underset{\displaystyle N}{N}}}{N}}-NH_2\ +\ 2CO_3^{2-}\quad\longrightarrow\quad N=N-\cdots+\ 2HCO_3^-\ +\ 2H_2$$

Scheme 1: *Coupling reaction of sodium 5,5'-azotetrazolate (SZT) over W, Mo co-doped BiVO$_4$ under visible light irradiation.*

The application of BiVO$_4$/WO$_3$ to the PEC dimethoxylation of furan has been performed at low applied bias using a Br$^+$/Br$^-$ mediator.[14] Et$_4$NBr, and Et$_4$NBF$_4$ as a co-supporting electrolyte, allowed the reaction to proceed in methanol with a Faradaic efficiency of up to 99% at +0.1 V vs. SHE. It is possible that for this reaction, the undesirable oxidation of methanol and the methoxylated product will be mediated directly by the photogenerated holed on the photoanode surface, however, at +0.4 V vs. SHE, it was found that the methoxylated product was afforded with a high Faradaic efficiency of 75%. The reason for this is that the PEC oxidation of furan proceeded via an indirect method; holes selectively oxidised Br$^-$ to Br$^+$, which rapidly reacted with furan to form the corresponding cation, which then reacted further with MeOH. It was noted that using Br$_2$ to produce Br$^+$ instead only gave a 12% yield, suggesting that the PEC oxidised species from Br$^-$ is probably from a Br$^+$-like species rather than Br$_2$.

Using a BiVO$_4$/WO$_3$ photoanode, Tateno *et al.* have employed N-hydroxyphthalimide (NHPI) as an electron transfer mediator, which is indirectly oxidised to the radical, phthalimide N-oxyl (PINO), which serves as a catalyst by retrieving a proton from the C-H bond scission of organic compounds, for the PEC oxidation of cycloalkenes to cycloalkenones (**Fig 3**).[8] Solar irradiation allowed the selective oxidation of cyclohexane to 2-cyclohexene-1-one to occur with a low applied bias and a Faradaic efficiency exceeding 99%; cyclopentene and cycloheptene were also oxidised with 73% and 93% efficiencies, respectively. What is also interesting here is that the C-H bond in the cycloalkenes and cycloalkenones is relatively inert and that, to the best of our knowledge, PINO has not yet been reported for PEC organic transformations. Moreover, several N-oxyl radicals and cycloalkenes could be realised via this method, indicating its future promise in organic synthesis, and that the NHPI is primarily oxidised on the surface of the photoanode, thus hindering unwanted reactions with other species in the mix.
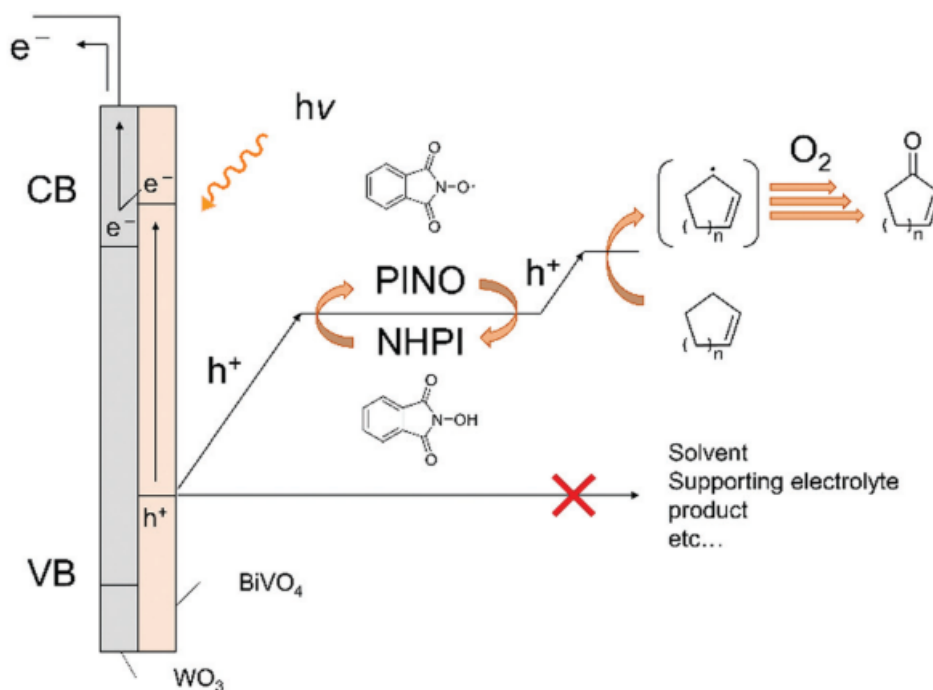
Fig 3: *Mechanistic illustration of the selective PEC oxidation of generic cycloalkenes to cycloalkenones, mediated by PINO/NHPI over a BiVO$_4$ (2.4 eV) photoanode with WO$_3$ as the electron collector. Reproduced from ref [8].*

Continuing with the use of BiVO$_4$ and NHPI, Wang *et al.* fabricated a PEC system for the P-H/C-H dehydrogenation cross-coupling reaction.[15] Such reactions are of interest because, firstly, they produce molecular hydrogen (important for energy applications) and secondly, they form C-P bonds in organophosphates for use in the areas of materials chemistry, agrochemistry and biochemistry. In an undivided cell, aBiVO$_4$ (working electrode), Pt (counter electrode), Ag/AgCl (reference electrode), ^{n}Bu$_4$NBF$_4$ (electrolyte), acetonitrile (solvent), and 0.2 equiv NHPI (mediator) were utilised, and the desired product was formed in 93% yield by 12 hrs of photoelectrolysis at a potential of +0.5 V vs. Ag/AgCl.. It was also reported that this methodology was applicable to a broad scope of substrates, affording a range of tertiary amines in yields ranging from 64-91%. Finally, as a comparison, the same reaction (**Scheme 2**) was performed in an electrochemical cell, employing a glassy carbon anode as the working electrode. A similar yield (88%) was obtained, however, a much larger external applied bias was required (1.5 V compared to 0.1 V for the PEC cell) to produce a 5.0 mA current, which translated to an almost 90% increase in the absence of light.
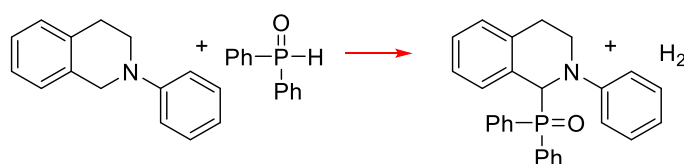
Scheme 2: *PEC P-H/C-H dehydrogenation cross-coupling reaction to reveal the formation of a C-P organophosphate bond.*

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Zhang *et al.* have reported the use of haematite as a photoanaode for the C-H amination of a range of aryl C-N containing molecules, including the late stage functionalisation of pharmaceutical compounds, performed in the absence of directing groups.[9] It appears that haematite (band gap 2.1 eV) was previously unexplored for PEC organic synthesis, and in this work, it was subsequently employed for the C–H/N–H coupling of anisole with pyrazole. Under conditions consisting of a blue LED (0.7 V) as the light source, a photocurrent of 2~3 mA cm^{-2}, ^{n}Bu$_4$NBF$_6$ as the electrolyte, a solvent system of HFIP/MeOH (4:1), and a reaction time of 10 h, the respective product was obtained in 75% yield with an *ortho/ para* ratio of 4:1. Replacing the electrolyte for LiClO$_4$ resulted in a yield of 77% and an enhanced *ortho* selectivity of 6:1. In contrast to this PEC reaction being performed in an electrochemical system, in which over-oxidation lead to trimerisation, no side products were detected (only unreacted species). This high *ortho* selectivity is rather unusual because even though both *ortho* and *para* configurations are expected, the *para* configuration should be favoured due to less steric hindrance, as outlined in **Scheme 3** and previously reported works[16,17] on organic PEC synthesis for electron-rich arene C-H amination, in which oxidation to a radical cation is followed by nucleophilic attack to the *para* position. In the case of haematite, photogenerated holes that oxidise the arene to an electrophilic radical cation allow it to react with pyrazole to form an intermediate species. Loss of a proton to afford a second intermediate followed by loss of an electron and another proton yields the amination product. These two protons are then reduced by the photoexcited electrons in haematite to form hydrogen gas. The reason the *ortho* product has been formed predominantly over the *para* product has been attributed to the HFIP hydrogen bonding with the *ortho* intermediate (**Scheme 3**) and thus, stabilising it.
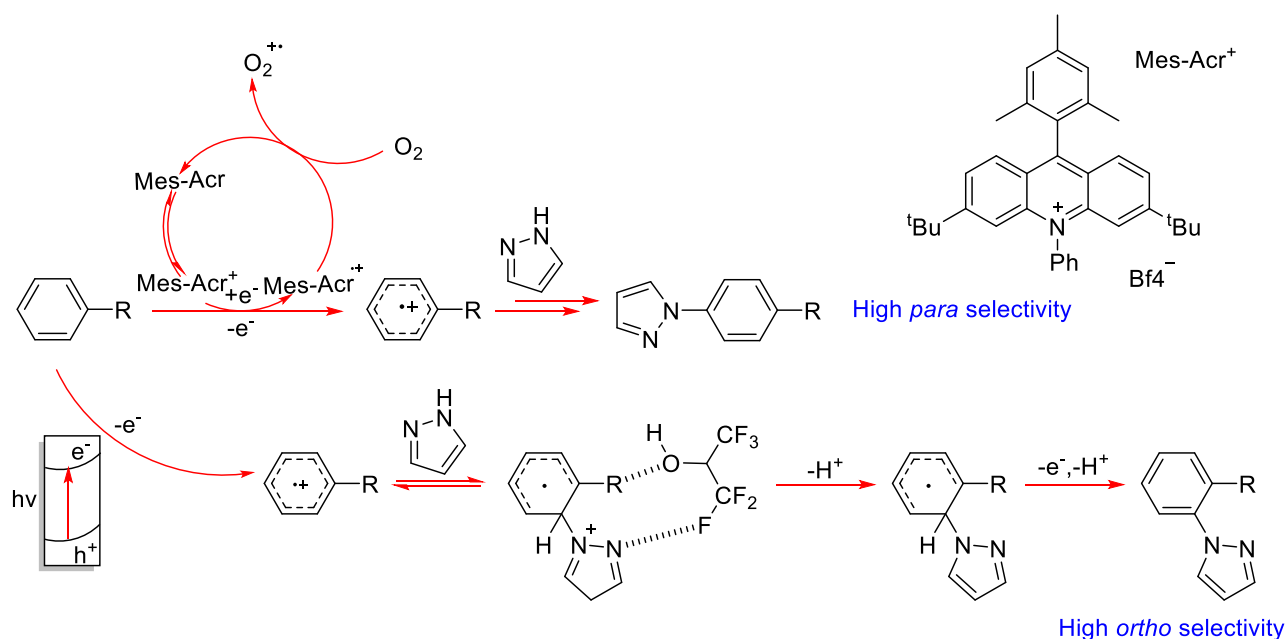
Scheme 3: *Mechanism for the PEC C-H amination resulting in the conventionally dominating para configuration and proposed mechanism for the formation of the ortho product due to hydrogen bonding (dashed lines) stabilising the intermediate.*

There is a desire to achieve organic syntheses of intermediate species that are important for commercial materials, such as nylon-6 and nylon-6,6 polymers for the textile industry. However, such methodologies rely on high temperatures are pressures. By utilising photoelectrochemistry,

Tateno *et al.* have taken the difficult to oxidise cyclohexane and subjected it to C-H activation (high dissociation energy of 439 kJmol^{-1}) under ambient conditions using visible light with porous WO_3 (~2.58 eV), a direct band gap semiconductor acting as the photoanaode, a Pt cathode and ^{t}BuOH/HNO_3 electrolyte, to form KA oil (ketone-alcohol oil), a mixture of cyclohexanol and cyclohexanone. In the dark, negligible production was observed; however, oil was produced with under illumination. Product formation occurred, even in the absence of an external applied bias, although the rate was very low (<8 mmolh^{-1}), but significantly increased with an applied bias to reach 41.2 mmolh^{-1} at 2.0 V. Moreover, no by-products (i.e. bicyclohexyls) were formed, and a high partial oxidation selectivity (99%) and Faradaic efficiency (76%) were achieved. Incident photon-to-current efficiencies (IPCE) were 57% and 24%, at 365 and 420 nm, respectively. Over a period of 5 h, 34 mmol of cyclohexanol, 67 mmol of cyclohexanone and only 7 mmol of CO_2 were produced.

In another study, Tang *et al*. performed the simultaneous production of hydrogen and 3-pyridinecarboxylic acid (3-PA) from the oxidation of 3-methylpyridine (3-MP) in aqueous media.[18] Their device consisted of a dual-chamber PEC cell with a WO_3 photoanode, a Pt wire cathode, and a proton exchange membrane to avoid the reverse reaction, as shown in **Figure 4**. Photogenerated holes could then oxidise the 3-MP to 3-PA on the WO_3 surface while the electrons reduced water into hydrogen at the Pt. The calculated E^O of 3-MP to 3-PA was found to be 0.93 V vs. RHE, compared to that of the water splitting which is 1.23 vs. RHE, therefore, indicating that this reaction is more thermodynamically favourable. The use of a $Cr_2O_7^{2-}/Cr^{3+}$ redox couple was also found to improve the device efficiency by acting as a mediator.
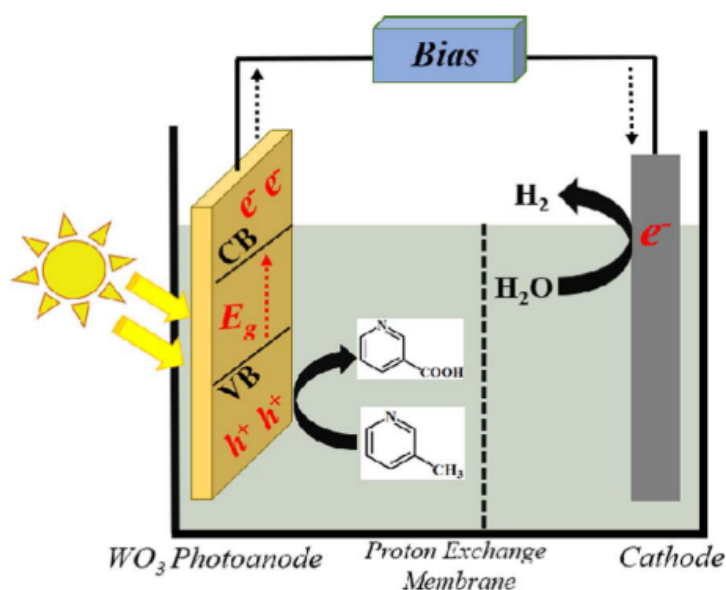

Fig 4. *Pictorial representation of a dual-chamber WO_3-containing PEC cell for the oxidation of 3-MP to 3-PA. Reproduced from ref* [18].

The PEC oxidation of organic substrates in non-aqueous media was performed by Li *et al.*[19] The first type of reaction tested was the selective alcohol oxidation of benzyl alcohol to benzaldehyde, and the second was the more difficult (since this type of reaction is typically done in the presence of toxic chemicals and precious metal catalysts) C-H oxidation of cyclohexene to cyclohexenone and tetralin to 1-tetralone. The PEC cell itself utilised $BiVO_4$ as the photoanode, MeCN as the

organic solvent, an LiClO$_4$ electrolyte, pyridine as the base, N-hydroxysuccinimide (NHS) (oxidation of NHS$^-$ to NHS• which abstracts a proton) as a hole transfer mediator, and an applied voltage of 0.8 V; all under AM 1.5G light (in the case of the C-H oxidation reactions, tert-butyl hydroperoxide, ^{t}BuOOH, was also added as an external oxygen source). It was found that photocorrosion of BiVO$_4$ in water was significantly larger than in MeCN (insignificant photocorrosion was observed), which is why this solvent was chosen for the PEC measurements. However, organic electrolytes increase the resistance of cell, requiring an additional voltage of *ca.* 20 mV in this case, which has been regarded as an acceptable energy penalty for a higher photoanode stability. Moreover, the use of sunlight was able to reduce the external applied electrical energy, compared to an electrochemical system, by 60%. Under the above conditions and a reaction time of 8 h, the PEC oxidation of benzyl alcohol to benzaldehyde was afforded in 41% yield, cyclohexane to cyclohexanone in 38% yield, and tetralin to 1-tetralone in 75% yield (93% conversion) after 24 h. While the yields of the first two are not satisfactory, the concept provides evidence for the feasibility of PEC synthesis in an organic media, as well as the combination of NHS with BiVO$_4$ for mediating redox reactions. Finally, the authors calculated that the overall solar-to-electricity efficiency of the cell was quite low at a value of 1.3%.

Conclusion and Future prospective:

The rational synthesis of organic compounds is one of the primary goals of green and sustainable chemistry. In this work, we have underlined the current status and future prospects of photoelectrochemical cells to drive the synthesis of organic compounds. Following on from here are four major aspects that will enable solar-induced organic transformations to become a broad subject of interest in near future:

1. **Photoelectrodes:** Fabrication and discovery of more well suited photoanodes which can absorb a boarder spectrum of visible light, such as those grown in nanostructured layers i.e. BiVO$_4$, GaN/ZnO, Cobalt phosphate, Al:GaN TaON, and Nb$_2$O$_5$ in addition to photocathodes like NiO, Al:SrTiO$_3$, and Cu$_2$O on transparent conducting oxides (TCOs), for example FTO deposited by magnetron sputtering, atomic layer deposition and chemical vapour deposition or chemically synthesised, high surface area nanopores that can be deposited on FTO by screen printing to achieve high quality films which can withstand longer time periods in aqueous electrolyte solutions and can play a vital role in various organic transformation reactions with enhanced efficiency. This method also opens up the novel prospects of interdisciplinary opportunities by employing higher quality nanostructured thin film photoanodes in organic synthesis. Cocatalyst deposition on photoanodes can potentially add more value to this process as cocatalysts can offer additional oxidation or reduction active sites, enhance the rate of surface reactions by reducing the activation energy and suppress electron-hole pair recombination. Moreover, the surface passivation of photoanodes can advance the PEC organic synthesis process as the semiconductor surface/interface is a noticeable region in PEC systems that can improve charge separation and maximise efficiency of the electrode, resulting in better conversions.

2. **Ambient sunlight for photovoltaics and clean synthesis:** These PEC based reactions need to be standardised to characterize and improve their performance under simulated solar light, in order to enable solar-induced organic transformations to become a reality under ambient sunlight and to reduce their energy dependence on conventional fossil fuel generated power. In the future, it is hoped that inexpensive, alternative sources such as third generation solar cells will be the

driving force for these reactions, operating in solar energy reliant systems, and therefore, underlining the significance of green chemistry in the synthesis of useful and valuable chemicals.

3. **Neutral pH:** A vast amount of organic molecules either operate in an acidic or basic medium, however, PEC oxidation and reduction offers another advantage in which a neutral pH can be accessed, offering a more profound, green chemistry pathway.

4. Organic/polymer semiconducting photoelectrodes: Over the last two decades, the optoelectronics industry has been revolutionized by the development of high-performance organic semiconductors, tempting researchers working in PEC systems to use efficient and stable p- and n-type organic/polymers as photoelectrodes. We believe this will offer another route in the developing roadmap of organic transformations powered by photoelectrochemistry.

PEC technology is still, in its infancy, but it offers prospects for the evolution of solar-induced organic transformations towards better, cheaper, higher efficiency and environmentally safer and sustainable alternative reaction methodologies.

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Tomas Hardwick *obtained his master's degree in chemistry in 2018 at Cardiff University, performing organic chemistry research focused on electrochemical organic synthesis in batch and flow. During such time he spent a year working on heterogeneous catalysis at the University of Florida in the Department of Physical Chemistry and Centre for Nanostructured Electronic Materials. He is currently a Ph.D. student in the Department of Materials in the University of Manchester working with the Advanced Nanomaterials Group, with research interests involving two-dimensional materials for photovoltaics and photoelectrochemistry*

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