

Artificial Photosynthesis: Faraday Discussion

Platinum group metals still important for superior photocatalytic activity

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Introduction

The Royal Society of Chemistry Faraday Discussions are a series of meetings focusing on rapidly developing areas of physical chemistry. Contrary to typical conferences, Faraday Discussions rely on the active participation of speakers and audience alike. Topics for each session are based on new research papers submitted specifically for the meeting. Audience participation is important because short presentations on each paper are followed by lengthy discussions, with all delegates free to ask questions and make comments. All questions and answers are recorded and later published in a Faraday Discussions volume. These conferences are a useful forum for documenting the current state of the art within a field of research.

The 2017 Faraday Discussion on artificial photosynthesis took place in Kyoto, Japan. This was noteworthy as it was the first time a Faraday Discussions meeting was organised in Japan. The three-day event from 28th February to 2nd March 2017 was hosted at the Ritsumeikan University Suzaku Campus, Kyoto. Some 100 delegates attended with approximately 30 speakers and close to 50 poster presentations. Topics covered all areas of artificial photosynthesis from biological

approaches, fundamental processes to molecular and inorganic assembly catalysts, as well as integration of systems for practical devices.

This review will discuss the role of platinum group metals (pgm) in the continuing drive to develop new catalysts for molecular and photoelectrochemical approaches to water splitting and carbon dioxide reduction.

Molecular Catalysts for Water Splitting

The ultimate goal of reducing the world's dependence on fossil fuels cannot be realised by laboratory-scale solutions alone, an increased collaboration with industry is required. To that end a number of industry experts attended the conference, bringing their perspective on the technical challenges in implementing large-scale production of solar fuels. Tohru Setoyama (Mitsubishi Chemical Science and Research Centre, Japan) detailed the state of the solar hydrogen industry. With a target of 10% solar to hydrogen conversion efficiency by 2021 industry has set researchers an ambitious goal (1). This will require greater focus in a field which has become divergent in its approaches to generating solar fuels.

In the context of molecular catalysts for water splitting it is apparent that pgms still offer the best overall performance. Current work has sought to build a better understanding of the mechanisms behind photocatalytic water splitting (**Figure 1**) and carbon dioxide reduction. Ruthenium-based catalysts continue to be favoured as a starting point for new catalysts. Now that the mechanistic understanding has improved, several research

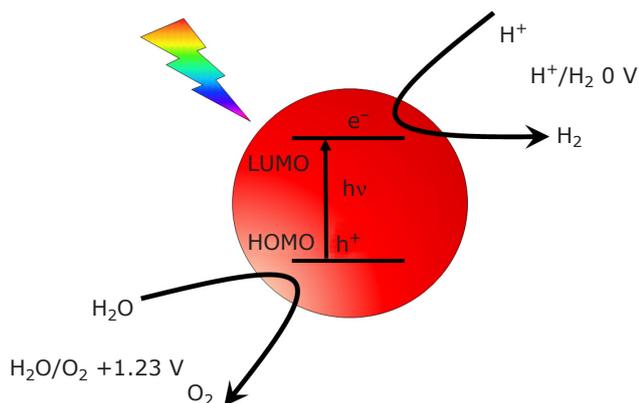


Fig. 1. Simplified scheme for photocatalytic water splitting using a molecular catalyst

groups are optimising the ligand environment around Ru in particular. This has led to several promising molecular systems for water splitting and CO_2 reduction.

Ru-based water-oxidation catalysts (WOC) have been extensively studied since the first example of an artificial WOC, in 1982, came in the form of a dinuclear Ru-complex, the well-known 'blue-dimer'. Over subsequent years there have been a large number of dinuclear and mononuclear Ru-based WOCs reported. In a systematic comparison of Group 8 metal complexes bearing the same pentadentate and monodentate ligands (Figure 2), Shigeyuki Masaoka *et al.* (2) (Institute for Molecular Science, Japan) contributed more evidence for understanding the basis for the excellent water-oxidation activity of Ru-based catalysts against iron and osmium complexes. It

was concluded that ligand substitution lability was a crucial factor in the design of future catalysts.

Revisiting Solar Fuels Production *via* Heterogeneous Catalysis

Hyunwoong Park *et al.* (3) (Kyungpook National University, South Korea) demonstrated photocatalytic production of molecular hydrogen using a ternary composite of platinum, cadmium sulfide and sodium trititanate nanotubes (TNT), Pt/CdS/TNT. The impetus for this work was to revisit solar fuels production *via* heterogeneous catalysis. Although CdS has in the past been studied as a photocatalyst, problems with decomposition and the need for a sacrificial electron donor or hole-scavenger prevented these systems from being effective.

With their sodium TNT composite the authors observed a six-fold increase in hydrogen evolution compared to a more traditional heterogeneous photocatalytic system, a Pt/CdS/ TiO_2 composite. H_2 evolution was shown to be exclusively from water splitting in an aqueous system containing 5 vol% 2-propanol (IPA) as a sacrificial electron donor. The Pt/CdS/TNT composite essentially protected the metallic Pt from oxidation and CdS from decomposition. Pt plays a key role as a co-catalyst in the system, promoting charge transfer. Pt is known to effectively catalyse H_2 evolution in CdS composites under visible light irradiation. However, the interplay between CdS, Pt and the sacrificial electron donor has led to disparate reports on the effectiveness of Pt as a co-catalyst.

The Pt/CdS/TNT system is more durable with respect to CdS decomposition. Isotopic analysis of the gasses evolved from the system gives a better

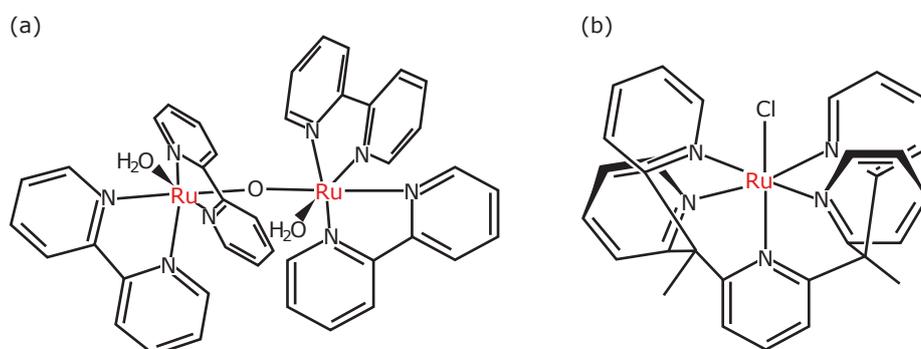


Fig. 2. First reported WOC: (a) the 'blue dimer'; and (b) pentadentate mononuclear Ru WOC from Masaoka *et al.* (2)

understanding of the mechanism for H₂ evolution. It is particularly important to note that at higher concentrations of sacrificial electron donor (>5 vol% IPA) not all the H₂ produced is from water splitting, but also from deprotonation of IPA. This might lead to an overestimation of H₂ produced in similar systems.

Photochemical Reduction of Carbon Dioxide

Developing photochemical systems for the reduction of CO₂ to carbon monoxide, methanol and other useful fuels remains highly desirable, but very difficult. Given the sheer stability of CO₂ (one-electron reduction potential of -1.91 V vs. normal hydrogen electrode (NHE)), this remains extremely challenging to realise photochemically. Reduction to CO and formic acid requires two electrons, therefore catalysts must be capable of multi-electron reduction in order to be effective.

Etsuko Fujita *et al.* (4) (Brookhaven National Laboratory, USA) investigated photochemical reduction of CO₂ to CO using [Ir(tpy)(ppy)Cl]⁺ derivatives. These iridium complexes are one of only a few known compounds able to photochemically reduce CO₂ without a sensitiser, as they absorb light in the ultraviolet (UV)-visible region. These complexes still require a sacrificial electron donor in order to function. The authors

used the [Ir(tpy)(ppy)Cl]⁺ catalyst as a starting point for new variants with electron-rich ligands. Previous studies had identified the strength of hydride donating species as key intermediates in the catalytic process.

On that basis the aim was to add electron-rich substituents (bis(benzimidazole)-phenyl or -pyridine) in place of bidentate (ppy) and tridentate (tpy) ligands with a view to creating strong hydride donors for products further reduced beyond formate and CO₂. It was found that while CO₂ could be selectively reduced to form CO, turnover numbers did not increase with increasing hydricity. The work highlights the difficulty in rational design of photocatalysts for CO₂ reduction. It is postulated that effects of the intermediate singly reduced and doubly reduced catalyst species need to be better understood going forward to reduce CO₂ more efficiently to CO, formate and beyond.

Osamu Ishitani and Yusuke Tamaki (5) (Tokyo Institute of Technology, Japan) also addressed the problem of CO₂ reduction to CO and formic acid, but with a supramolecular approach. In their supramolecular system an asymmetric bis-tridentate Ru(II) complex functions as a photosensitiser and a Ru(II) carbonyl complex as the catalyst (**Figure 3**). The work builds on previous studies where supramolecular catalysts were coupled to semiconductor surfaces. The authors aim to attach the catalyst to a semiconductor and

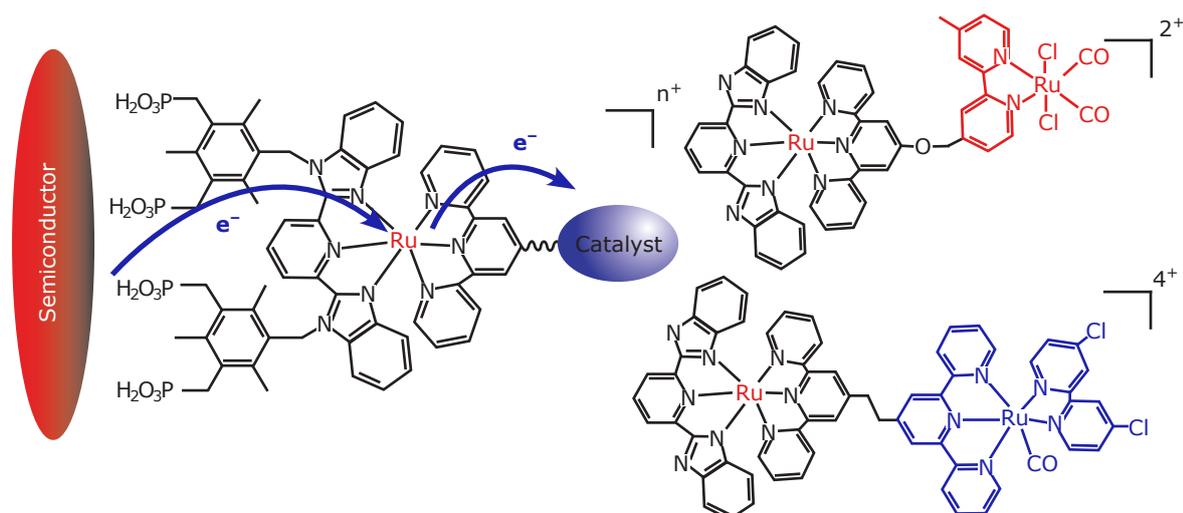


Fig. 3. Concept of a hybrid supramolecular catalyst system with photocatalyst/sensitiser. Coupling the sensitiser to [Ru(Clbpv)(CO)] (blue) selectively reduces CO, or [Ru(CO)₂Cl₂] (red) selectively reduces formic acid. The remaining ligand on the catalyst is the bridging ligand (Adapted from (5) with permission of The Royal Society of Chemistry)

increase the oxidative power in a future study. Here the properties of the catalyst-sensitiser unit have been characterised. Coupling the sensitiser to a catalyst *via* a bridging ligand helps overcome previous problems with back electron transfer. Furthermore, use of the asymmetric tridentate Ru(II) complex as a sensitiser was important since it has an excited state lifetime long enough ($^3\text{MLCT } \tau \approx 30 \text{ ns}$) to transfer an electron to the catalyst. This integrated supramolecular approach means even weak electron donors such as methanol and water can be used to selectively reduce CO_2 to formic acid and CO.

Concluding Remarks

The meeting clearly demonstrated that, as a community, the approaches to artificial photosynthesis have become quite varied. Over a number of years now there has been a drive towards replacing pgms as catalysts for water splitting and light-harvesting molecules with Earth-abundant alternatives such as iron and manganese. Researchers keep returning to pgms though, because of their superior catalytic activity and to gain further mechanistic insight into water splitting and CO_2 reduction. Discussions during the sessions noted that if there is to be progress towards some of the goals industry has set for solar fuels production on a mass-scale, then the scientific community is going to have to agree on a more concentrated direction forward. The cost of the pgms cannot be the main impetus for seeking Earth-abundant alternatives if the alternatives fall greatly short in terms of performance in real devices. In the future there may well need to be far greater focus on one class of catalysts. The viewpoint of representatives from industry highlighted infrastructure considerations and full lifecycle analysis as driving forces for industrial-scale solar fuels production.

A recurring theme during the meeting was the effects of temperature on catalytic activity in electrocatalytic and photocatalytic systems. This is very closely linked to practical device design. There is more to be learnt about the dynamics of molecular catalysts at different temperatures. Indeed practical devices may operate at a range of elevated temperatures, where catalyst activity may be quite different. Finally, as noted by Daniel Nocera and others, while solar fuels production must overcome the current reliance of fossil fuels, no one-size-fits-all solution is capable of overturning the overbearing economic sway of the fossil fuels industry. Change may well come with government intervention in the form of carbon taxation for example. Until then the enormous cost of replacing fossil fuel infrastructure will continue to be an obstacle. This shows the need for closer co-operation with industry, which no doubt will continue in future meetings. In the meantime the fundamental research into artificial photosynthesis seen at meetings like Faraday Discussions will continue to underpin future innovations.

"Faraday Discussion: Artificial Photosynthesis" 2017 is currently in press. The volume will be made available in due course.

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The Reviewer



Joshua Karlsson graduated from the University of York, UK, in 2013 with a BSc in chemistry, and an MRes in Green Chemistry from Imperial College London, UK, in 2014. He is now in the final year of a PhD project under the supervisor of Professor Anthony Harriman at the Molecular Photonic Laboratory, Newcastle University, UK. His research revolves around investigating the fundamental photophysical properties of fluorescent dyes in the far-red spectral region and applying this knowledge in the contexts of super-resolution fluorescence microscopy and organic solar cells.