Synthetic approaches to artificial photosynthesis: general discussion

Anton-Garcia, D.; Apfel, U.-P.; Andrei, V.; Aitchison, C.M.; Badiani, V.; Beller, M.; ... ; Zwijnenburg, M.A.

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Synthetic approaches to artificial photosynthesis: general discussion

Catherine M. Aitchison, Virgil Andrei, Daniel Antón-García, Ulf-Peter Apfel, Vivek Badiani, Matthias Beller, Andrew B. Bocarsly, Sylvestre Bonnet, Peter Brueggeller, Christine A. Caputo, Flavia Cassiola, Simon T. Clausing, Andrew I. Cooper, Charles E. Creissen, Víctor A. de la Peña O'Shea, Wolfgang Domcke, James R. Durrant, Michael Grätzel, Leif Hammarström, Anna Hankin, Marta C. Hatzell, Ferdi Karadas, Burkhard König, Moritz F. Kuehnel, Sarah Lamaison, Chia-Yu Lin, Marcelino Maneiro, Shelley D. Minteer, Aubrey R. Paris, Ernest Pastor, Chanon Pornrungroj, Joost N. H. Reek, Erwin Reisner, Souvik Roy, Constantin Sahm, Ravi Shankar, Wendy J. Shaw, Sergii I. Shylin, Wilson A. Smith, Katarzyna Sokol, Han Sen Soo, Reiner Sebastian Sprick, Wolfgang Viertl, Anastasia Vogel, Andreas Wagner, David Wakerley, Qian Wang, Dominik Wielend and Martijn A. Zwijnenburg

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Moritz F. Kuehnel opened a discussion of the paper by Andrew I. Cooper: What do you know about the HOMO and LUMO localisation on the polymers? I suppose this is strongly affected by introducing heteroatoms such as sulfur, and that this causes the changes observed when oxidising the thiophene to sulfolane moieties. Can you use different heteroatoms to tweak the redox potentials?

Andrew I. Cooper answered: Yes – by changing the heteroatom one can change the catalytic activity, but this can also change a variety of other things such as the surface hydrophilicity and (in some cases) the polymer molecular weight, or, in the case of networks, the surface area. As such, it is often unclear whether these effects come from changes to the redox potentials or a variety of factors.

Moritz F. Kuehnel asked: How much is known about the residual palladium in the polymer? What do you know about its environment, which I assume will depend on functional groups in the polymer backbone, *e.g.* donor groups? I am wondering if the observed differences in activity for different polymers are a result of the different palladium environments, rather than other, more easily determined factors. such as the band gap, *etc.* Do you have any EXAFS data?

Andrew I. Cooper responded: No, no EXAFS data as yet, but the palladium metal can vary in size from a few nanometers (or even palladium clusters) up to 50 nm or so. Ian McCulloch, James R. Durrant and coworkers have shown in ref. 1 that palladium can be catalytically active in such materials at very low concentrations. In their studies, very low palladium concentrations (<40 ppm) have an effect on the photocatalytic hydrogen evolution rate.

1 J. Kosco, M. Sachs, R. Godin, M. Kirkus, L. Francas, M. Bidwell, M. Qureshi, D. Anjum, J. R. Durrant and I. McCulloch, *Adv. Energy Mater.*, 2018, **8**, 1802181.

Virgil Andrei enquired: The polymers employ residual palladium from the Suzuki–Miyaura coupling as the hydrogen evolution co-catalyst. Have you considered using molecular catalysts to expand the scope of the photocatalysis towards CO_2 reduction? The polymers possess aromatic units; therefore, molecular catalysts may be easily attached to the polymeric backbone *via* π–π stacking interactions.

Andrew I. Cooper responded: Yes, we are working on this – for example, by introducing bipyridyl metal binding sites into the polymers.

James R. Durrant commented: I am intrigued that the most active polymer you show appears to be very hydrophobic. For proton reduction photocatalysis I would have expected that some degree of polymer hydrophilicity would be preferred. Could you comment on this?

Andrew I. Cooper responded: Hydrophilicity is an important variable, but it is one such factor – the hydrogen evolution rate is also affected by the band gap, the energy levels, particle size, surface area, and the level of precious metals in the material, which act as co-catalysts. A big difficulty in designing these materials is that no single variable dominates the catalytic activity (see for example: ref. 1).

1 Y. Bai, L. Wilbraham, B. J. Slater, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *J. Am. Chem. Soc.*, 2019, **141**, 9063–9071.

Wendy J. Shaw remarked: I am curious as to whether secondary/tertiary structures (similar to biopolymers) have been investigated and what their role might be in controlling reactivity?

Andrew I. Cooper responded: No, only in the context of crystalline COFs and amorphous analogues, where strong differences in catalytic activity are observed, *e.g.* as in ref. 1. It is hard to control secondary/tertiary structure in these rigid polymers.

1 X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Nat Chem.*, 2018, **10**, 1180.

Michael Grätzel commented: I assume that a sacrificial donor was used in the light driven hydrogen evolution process. Could Professor Cooper please provide the chemical structure of the donor? I wonder whether the hydrogen produced under light arises from the reduction of water or from the sacrificial donor. Could Professor Cooper also show the action spectrum for the hydrogen generation to see whether it matches the absorption spectrum of the ladder polymer acting as a sensitizer?

Andrew I. Cooper responded: Yes, we used triethylamine or triethanolamine generally, or in some cases ascorbic acid, but we have also tested non-hydrogen containing donors, such as Na_2S, to exclude the possibility of the hydrogen coming from the donor.

Ravi Shankar opened a discussion of the paper by Martijn A. Zwijnenburg: The screening method that you have applied for polymeric photocatalysts is very interesting. Is there scope to apply or expand this screening method towards other types of catalysts, such as porous catalysts?

Martijn A. Zwijnenburg responded: Our approach is specific for photocatalysts but other groups are working on similar approaches for other material classes, including porous materials.

Burkhard König commented: Conjugated polymers show a specific conjugation length. How many repeating units do you have to consider in your evaluation of polymer photocatalyst properties to describe them well by computational methods?

Martijn A. Zwijnenburg answered: Yes, indeed. In our experience oligomeric models with a length of twelve units, as used in this work, provide approximately converged properties with respect to oligomer length.

Wendy J. Shaw asked: What metrics are the computational results determined by? What makes a good catalyst? If you (and Professor Cooper) do not know what is bad then how do you know that you are not missing something?

Martijn A. Zwijnenburg answered: We know that a good photocatalyst should at least absorb visible light and have sufficient driving force for all desired solution reactions, proton or CO_2 reduction and water or sacrificial electron donor oxidation. What we know less about is what other factors are (the most) important (*e.g.* wettability, reaction kinetics, and charge–carrier and exciton transport), what the best (computational) descriptors for these additional factors are, and the nature of the interplay and trade-offs between the different properties. However, ignoring what we do not fully understand, this still means that by predicting the optical gap and potentials of materials we can rule out many of them by computational screening and only concentrate on the more promising remaining ones experimentally. To paraphrase Frank Westheimer: A couple of months in the laboratory can frequently save a couple of hours of computer time. Another use of (computational) screening in my opinion is to gain an understanding of how photocatalyst properties are interconnected by generating data sets that are large enough to extract inter-property correlations.

Wolfgang Domcke said: The exciton binding energy can be quite large in these polymeric materials and therefore it is an important parameter. Will you come up with specific numbers in the future?

Martijn A. Zwijnenburg responded: While we have not done so here, the exciton binding energy could in principle be approximated from the difference in the fundamental gap, itself defined as the difference between a polymer's ionisation potential and electron affinity, and its optical gap. In previous work (ref. 1) we approximated the exciton binding energy for an exciton in the polymer bulk and near the polymer–water interface using DFT and found values of 1200 and 170 meV, respectively. The fact that even the latter value is much larger than the kT at room temperature (26 meV) suggests that excitons in the polymer photocatalyst likely dissociate on the polymer–water interface or polymer–polymer interface in the case of a heterojunction, with the electron and hole after dissociation ending up in different phases.

1 P. Guiglion, C. Butchosa and M. A. Zwijnenburg, *Macromol. Chem. Phys.* 2016, **217**, 344.

Marcelino Maneiro opened a discussion of the paper by Ferdi Karadas: I think that cyclic voltammetry would shed more light on the characterization of your system, and even on its catalytic mechanism. Have you tried to perform cyclic voltammetry on your Ru–P4VP–CoFe dyad? In relation to the catalytic activity, do you have any evidence that water is oxidized at the cobalt sites?

Ferdi Karadas replied: I agree that cyclic voltammetric studies would definitely help to characterize the assembly in more detail. Such measurements, however, were not performed mainly because the assembly does not dissolve in water and coating this polymeric assembly on an FTO electrode *via* conventional methods was not successful.

The identity of the catalytic site was not investigated in this study. The origin of the catalytic site has been investigated previously and it is well-established in Prussian blue systems that hexacyanometal sites are not catalytically active sites and that it should be the cobalt sites that are coordinated to at least one water molecule. Please check our recent papers (ref. 1 and 2).

1 T. G. U. Ghobadi, E. A. Yildiz, M. Buyuktemiz, S. S. Akbari, D. Topkaya, Ü. Isci, Y. Dede, H. G. Yaglioglu and F. Karadas, *Angewandte Chemie Int. Ed.*, 2018, **57**, 17173.
2 E. P. Alsaç, E. Ülker, S. V. K. Nune, Y. Dede and F. Karadas, *Chem.: Eur. J.*, 2018, **24**, 4856.

Matthias Beller enquired: Following on from the previous question, how sure are you about the stability of this system? Did you compare it with other systems?

Ferdi Karadas replied: The ruthenium chromophore is connected to the Prussian blue (PB)-type water oxidation catalyst in our study. We also performed photocatalytic studies with a regular PB system in the presence of a ruthenium chromophore, which is not connected to PB. Previous studies in the literature as well as our photocatalytic studies and post-catalytic characterization measurements suggest that the connected assembly exhibits a much higher stability.

Michael Grätzel asked: Professor Karadas stated that his $Co(CN)_6$ Prussian blue-type catalyst remained intact during his reaction as a catalyst for the oxidation of water to oxygen. However it appears unlikely that this is the case for the catalyst molecules exposed to water that are actively involved in the oxygen evolution reaction. Rather, they are expected to be converted to cobalt oxides which in turn will catalyze the water oxidation reaction.

Ferdi Karadas answered: Prussian blue analogues (PBAs) are non-oxide based coordination networks, which make them way more stable than molecular catalysts. It should also be noted that the solubility product of PBAs is much lower than those of oxides due to the highly sigma-donating nature of the cyanide ligand, which leads to the formation of a strong M–CN–M' coordination mode. Furthermore, our XPS studies did not reveal any possible formation of oxides. The stability of PBAs have been studied comprehensively in ref. 1 and 2 as well.

1 L. Han, P. Tang, Á. Reyes-Carmona, B. Rodríguez-García, M. Torréns, J. R. Morante, J. Arbiol and J. R. Galan-Mascaros, *J. Am. Chem. Soc.*, 2016, **138**, 16037.

2 E. P Alsaç, E. Ülker, S. V. K. Nune, Y. Dede and Ferdi Karadas, *Chem.: Eur. J.*, 2018, **24**, 4856.

Catherine M. Aitchison queried: What do you think is the rate-limiting step in the system and have you tried to optimise the ratio of the components (*i.e.* sensitizer to polymer to catalyst)? Do you think this would also be important for stability given that you mention that a possible deactivation pathway of the catalyst is poisoning by photosensitizer ligands?

Ferdi Karadas replied: We have not performed any experiments to investigate the rate-limiting step. It could, however, be speculated that the rate-determining step could be the activation of the catalytic cobalt sites given its high overpotential. Within the project, two different assemblies with different stoichiometric ratios of Ru : Fe have been prepared. Since their performances are comparable only one of them was reported, so our preliminary studies do not indicate any correlation between the ratio of the components and the stability or performance of the catalyst.

Andrew B. Bocarsly asked: Following up on Michael Grätzel's question, how certain are you that the outer surface of the material is the catalysis site? Cyanide bridged cyanometalate complexes are known to form microporous structures. Thus, your substrate can penetrate into the interior of the cyanometalate layer. Furthermore, these materials tend to be rather defective with open coordination sites, thus interior catalytic sites may be available. Your materials may have some similarity to the $[Ru(bpz)_3]^{2+}$/cyanometalate layered structure discussed in ref. 1.

1 C. Hidalgo-Luangdilok and A. B. Bocarsly, *Inorg. Chem.*, 1990, **29**, 2894.

Ferdi Karadas answered: Thanks for sharing this paper. We are certain that cobalt sites that are coordinated to at least one water molecule should be catalytically active sites and we have previously shown in ref. 1 that this type of active cobalt site can be increased by incorporating polymers to this chemistry. The polymeric moiety probably increases the number of defective cobalt sites, as suggested, by decreasing the dimensionality of the Prussian blue structure. These defective sites are also known to occur in the interior of the network. We have also performed porosity studies on these polymer–PB hybrid structures (which is not reported in this manuscript), which show that their microporous behavior disappears since the polymeric groups probably block the microchannels. So even if there is a considerable number of active cobalt sites in the bulk of the material, these are not accessible. Overall, polymeric groups decrease the dimensionality of the PB structures at the expense of blocking the microchannels.

1 M. Aksoy, S. V. K. Nune and F. Karadas, *Inorg. Chem.*, 2016, **55**, 4301.

Reiner Sebastian Sprick addressed all of the presenters: When using organic polymers as photocatalysts stability is a concern, particularly when performing water oxidation. Would you be able to comment on this and have you performed experiments to explore this?

Martijn A. Zwijnenburg responded: The stability of polymer photocatalysts when using a sacrificial electron donor (SED) does not seem to be an issue (see ref. 1), however this might be different when oxidising water rather than a SED, especially if the former has sluggish kinetics. Supporting evidence for this hypothesis comes from work in the literature on a polymer consisting of triazine units linked by disulfide bridges (see ref. 2). This material is reported to stably evolve hydrogen in the presence of a SED but to photocorrode when using pure water.

1 R. S. Sprick, B. Bonillo, R. Clowes, P. Guiglion, N. J. Brownbill, B. J. Slater, F. Blanc, M. A. Zwijnenburg, D. J. Adams and A. I. Cooper, *Angew. Chem. Int. Ed.*, 2016, **55**, 1792.
2 Z. Zhang, J. Long, L. Yang, W. Chen, W. Dai, X. Fu and X. Wang, *Chem. Sci.*, 2011, **2**, 1826.

Ferdi Karadas answered: Our post-characterization studies mainly focused on the stability of the metal sites and whether they were transformed to any oxide under photocatalytic conditions. No special method has been performed to explore the stability of the polymer. The visual observation of the powder suspension, however, reveals that the suspension is colorless even after the photocatalytic experiment. This implies that none of the ruthenium fragment went into the solution. Therefore, even if the polymeric chain is broken during the photocatalysis, it was limited and did not lead to disconnection of the chromophore from the catalyst. The maintenance of the activity for six cycles also supports this hypothesis.

Matthias Beller followed this by asking: The sacrificial reductant plays a significant role. We get what we screen for – we screen for the best catalyst that works, *e.g.* triethanolamine, ammonium nitrate. How much can we learn from this for a real system? In the long term? Should we all focus on electrocatalytic reactions?

Martijn A. Zwijnenburg replied: It is undoubtedly true that the use of sacrificial electron donors (SEDs) biases the results and that one in the long term runs the risk of optimising a photocatalyst for oxidising a SED instead of water. In the short term, however, I still see a good case for the use of SEDs in photocatalyst discovery. For example, one would not want to miss a potentially promising photocatalyst system for overall water splitting because in the absence of the ideal co-catalyst water oxidation is too sluggish for any activity to be observed.

Ferdi Karadas answered: Since there are many possible systems to target and since the preparation and analysis of each of these systems is a tedious task, the use of a sacrificial agent is a practical solution for the sake of an efficient use of time. This solution, of course, comes with the expense of moving away from real condition analysis, which could give results beyond the ballpark or lead to wrong directions in certain cases. Thus, researchers should make their own risk analysis to choose the ideal conditions to test their systems.

Christine A. Caputo asked Martijn A. Zwijnenburg: There is a large molecular space to explore computationally. How many experimental validation points do you think you need to provide confidence that your approach is robust?

Martijn A. Zwijnenburg responded: Good question. As, as it stands, we do not predict photocatalytic activity as such but rather the materials properties that underlie it, we typically benchmark our ability to predict those. In terms of the number of validation points, the more the better. This is simple for some properties, *e.g.* the optical gap, as UV-Vis spectra are measured routinely, but harder for other properties, *e.g.* the ionisation potential and electron affinity of polymers, the measurement of which requires very specialized equipment, and as a result values have only been reported for a very limited set of polymers in the literature.

Dominik Wielend said: You have mentioned at the end of your paper that one of your future goals is the prediction of intermolecular properties like charge transport, *etc.* My question is, if you could estimate trends (maybe just qualitatively), which polymer combinations might tend to form intermolecular interactions (either stacking, which might be influenced by a possible bent structure of the polymer, or interactions similar to hydrogen-bonded pigments)?

Martijn A. Zwijnenburg responded: Thanks, that is an interesting suggestion; something we cannot do as yet but might be worth looking into in the future. In general, *a priori* predicting how molecules pack in the solid state is a very difficult problem, especially for amorphous or poorly-crystalline materials, like most polymers. The extent to which a more approximate approach might work will probably be controlled by how strongly a given property depends on the exact details of the packing and/or how common a particular packing motif is.

Joost N. H. Reek asked: With your new computational strategy you can evaluate many compounds, which is great. It is, however, possible that at the end you will have found a polymer with great properties that cannot be synthesised. So do you plan to implement any strategies to also take into account the synthetic availability?

Martijn A. Zwijnenburg answered: As for this work we typically consider commercially available monomers in combination with coupling chemistry that is experimentally known to be quite resilient, we are not so worried about synthetic accessibility here. In general, however, this is a very pertinent point, which several groups are trying to address. A good example from the literature is the work by Gómez-Bombarelli *et al.* on materials for the emissive layer of organic light-emitting diodes (ref. 1).

1 R. Gómez-Bombarelli, J. Aguilera-Iparraguirre, T. D. Hirzel, D. Duvenaud, D. Maclaurin, M. A. Blood-Forsythe, H. S. Chae, M. Einzinger, D.-G. Ha, T. Wu, G. Markopoulos, S. Jeon, H. Kang, H. Miyazaki, M. Numata, S. Kim, W. Huang, S. I. Hong, M. Baldo, R. P. Adams and A. Aspuru-Guzik, *Nat. Mater.* 2016, **15**, 1120.

Joost N. H. Reek posed to Ferdi Karadas: In your approach you are using polymers to which the catalyst and the chromophores are attached in a random fashion. In nature all of the components required for efficient photosynthesis are highly organised and well positioned with respect to one another. Of course it is nice that you show that this random organisation does lead to photo driven water oxidation, but it is unclear what the efficiency is (maybe only a small fraction of the components is sufficiently organised to be active). Can you comment on the efficiency (do you know this?), and do you think we need to develop strategies that allow for better spatial control of the components, for example by using supramolecular assembly?

Ferdi Karadas replied: I agree that the organisation of the components in an assembly is of crucial importance for better charge separation and efficiency. Interrogation of the efficiency or methods for improving the efficiency, although important, is beyond the scope of this study. It should be noted that the main objective of this proof-of-concept study is only to show that photosensitizers can be connected to a water oxidation catalyst *via* cyanide chemistry and that the chromophore is more stable in such an assembly. Given the results, our recent efforts have now been dedicated to the addition of each of these chromophores *in situ* on a semi-conductor. As suggested, the use of supramolecular assemblies can also provide an alternative synthetic pathway towards this goal.

Simon T. Clausing addressed all of the presenters: Andrew and Martijn presented polymers that are designed to fulfil all roles for photocatalytic hydrogen generation at once: light-harvesting, electron relay, a hydrogen evolving catalyst, and interface to water. It has been noted by Andrew that if you change one parameter to make it more efficient, you "break" another. Would it therefore not be better to focus on developing polymers that can, for example, be wettable light-harvesters with good electron relay functionality, and supply an external catalyst? Or have a catalytically active polymer, but supply an external photosensitizer? Ferdi showed a system like that; is that not an approach that might lead to quicker results, as it is modular by design?

Andrew I. Cooper responded: Yes, this is a very good idea in principle and recently we've been looking at more modular approaches. Putting the modules together again becomes complex, though...

Martijn A. Zwijnenburg replied: Indeed, using a composite rather than one polymeric material as photocatalyst is probably a promising strategy. One could actually argue that the commonly used polymers (inadvertently) loaded with metal nanoparticles are already examples of such composites, as well as the polymer–polymer and polymer–oxide heterojunctions reported in the literature. Moving from single materials to composites, however, could be a double-edged sword. The same complexity that makes it possible to independently optimise processes/properties will also make the workings of a composite photocatalyst more difficult to study and understand.

Ferdi Karadas added: As in natural photosynthesis, I believe that the preparation of a multifunctional assembly, wherein each component (chromophore, catalyst, donor, acceptor, *etc.*) is assigned for a special task, could be a viable approach for better efficiency. However, the field still needs new assemblies and proof-of-concept studies to explore its boundaries and establish its foundations. So even assemblies with lower efficiencies could help us learn more about this process.

Ernest Pastor addressed Martijn A. Zwijnenburg: Do you have any thoughts on the mechanistic role of the scavenger in these systems? For example in CO_2 reduction with molecular complexes it is proposed that the TEA or TEOA can participate in the mechanism at several points as you can form very reactive radicals. This could also affect the stability of the compounds.

Martijn A. Zwijnenburg answered: My hypothesis is that, in the case of TEA, the mechanism involves outer-sphere electron transfer from TEA in the first step and its singly-oxidised deprotonated counterpart in the second step. The latter is indeed very reactive in the sense that it is strongly reductive (predicted potential < -2.5 V *vs.* SHE at pH 11.5, the likely pH of a TEA solution, compared with +0.7 V for the first oxidation step and -0.7 V for the overall oxidation of TEA under the same conditions, see ref. 1 and 2). From a thermodynamic perspective this suggests that the first oxidation step will act as an effective kinetic barrier that needs to be overcome for overall oxidation of TEA to occur and that the second oxidation step is likely to be very fast. Beyond this we currently have very little mechanistic insight, something that hopefully will change in the near future.

1 R. S. Sprick, C. M. Aitchison, E. Berardo, L. Turcani, L. Wilbraham, B. M. Alston, K. E. Jelfs, M. A. Zwijnenburg and A. I. Cooper, *J. Mater. Chem. A*, 2018, **6**, 11994.
2 M. Sachs, R. S. Sprick, D. Pearce, S. A. J. Hillman, A. Monti, A. A. Y. Guilbert, N. J. Brownbill, S. Dimitrov, X. Shi, F. Blanc, M. A. Zwijnenburg, J. Nelson, J. R. Durrant and A. I. Cooper, *Nat. Commun.*, 2018, **9**, 4968.

Andreas Wagner asked Andrew I. Cooper: Is the difference in the stacking of the polymers dependent on their hydrophobicity? Could this influence the number of active sites and thereby explain differences in reactivity? Have you tried to use, *e.g.* circular dichroism to study the "folding" or stacking of these polymers in solution?

Andrew I. Cooper answered: We have not used circular dichroism. These polymers are mostly semi-crystalline at best; other materials such as covalent organic frameworks are much more crystalline (as shown in ref. 1) and also porous.

1 X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W.-H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Nature Chemistry*, 2018, **10**, 1180.

Erwin Reisner addressed all of the speakers: Our community is still mostly optimising photocatalytic half-reactions using sacrificial electron donors and acceptors, which causes the problems just discussed and they also need to be ultimately removed to catalyse useful closed redox cycles. Also, single light absorber photocatalyst systems have lower theoretical solar-to-fuel conversion efficiencies than dual light absorber systems and work by Domen, Kudo, Abe and others has previously shown that photocatalytic systems using semiconductor particle pairs can be constructed with suitable reversible redox shuttles. I would therefore like to hear your opinion on shifting the emphasis of our efforts to optimising our half-reactions using *reversible* redox shuttles rather than *irreversible* sacrificial donors. Optimising photocatalytic half-reactions with reversible donors is more challenging as it also introduces issues with back-reaction, but would in principle allow the coupling of individually optimised half-reactions *via* a reversible mediator to produce a functional closed redox system.

Andrew I. Cooper responded: I think this is absolutely the right way forward. As previously mentioned at the meeting, "you get what you screen for". I think there is an urgent need to move away from sacrificial reagents, unless (perhaps) these are coupled to biome schemes, waste degradation, *etc.*, and hence additively useful.

Martijn A. Zwijnenburg replied: I agree, two materials coupled together in Z-scheme by a reversible redox mediator is a strategy worth pursuing. From a computational perspective, this is something we could readily screen for using the methodology described in our contribution. In the defence of sacrificial electron donors, use of them has allowed Prof. Cooper's group and us to demonstrate that hydrogen evolution activity is quite a common property of conjugated polymers, something I suspect few people would have expected to be the case five years ago.

Erwin Reisner continued: Following on from the previous discussion on avoiding sacrificial reagents and developing closed redox cycles, I'd be curious to hear from the delegates about suitable redox shuttles (such as those developed by Domen, Abe, Kudo *et al.*), and recent progress on coupling semiconductor powders with reversible mediators for solar fuel synthesis. This topic may require more attention to allow progress using suspension/solution systems.

Joost N. H. Reek answered: I fully agree on this and we are currently looking into this. In fact, it is the central topic of poster 22 presented by Didjay Brugman.

Michael Grätzel commented: The groups of Professor Anders Hagfeldt (now at EPFL) and Professor Licheng Sun at Uppsala University have developed Cu(I) complexes acting as redox shuttles that produce very high photo-voltages exceeding 1.2 V in dye sensitized solar cells. The ligands of these complexes are engineered to conserve a nearly tetrahedral configuration upon oxidation to the corresponding Cu(II) complexes. These systems mimic the natural redox relays present in copper proteins which are coordinatively bound to histidine moieties and show very high electron exchange rates.

Víctor A. de la Peña O'Shea enquired: The use of polymers in the photocatalytic reactions is a very important challenge, where different reaction media, electron donors, illumination sources and many other parameters have been used to improve the photocatalytic activity. What is your opinion about the redox chemical reactions that occur over the catalytic surfaces? Are the active sites well defined?

Andrew I. Cooper answered: We do not know much about the specific active sites at present – it is possible that specific functional groups play a catalytic role, but as yet there are no mechanistic studies to confirm that.

Martijn A. Zwijnenburg added: Understanding the mechanism by which polymer photocatalysts can evolve hydrogen and/or oxygen is, in my opinion, the next big challenge in the field. Not much is known with certainty in this area. One can hypothesize that for polymers loaded with palladium and platinum nanoparticles, either added intentionally or as the remains of the catalysts used to synthesize the polymers, the mechanism involves electron transfer to these nanoparticles, which then reduces the protons and evolves the hydrogen. Indeed there is experimental evidence in ref. 1 that, at least for some polymer photocatalysts, removing any traces of palladium results in the disappearance of any hydrogen evolution activity. However, there also reports in the literature that appear to suggest that certain polymers might be able to evolve hydrogen in the absence of any noble metal.

1 J. Kosco, M. Sachs, R. Godin, M. Kirkus, L. Francas, M. Bidwell, M. Qureshi, D. Anjum, J. R. Durrant and I. McCulloch, *Adv. Energy Mater.*, 2018 **8**, 1802181.

Wolfgang Viertl opened a discussion of the paper by Wendy J. Shaw: How strong do you estimate the influence of the hemilabile coordinations from the outer coordination sphere to the metal centre to be? Do you think that oxygen from the amino acid residues can coordinate to the metal hydride or the metal centre itself without any additional hydride? Are any stabilisation effects considered here?

Wendy J. Shaw answered: Given the likely flexibility of the ligand, it is unlikely that the COOH or COOMe groups are binding to the active site. In a related version of the catalyst, which has significantly limited structural flexibility, we think we see this under very restricted conditions. Although we have not seen any evidence by NMR or electrochemistry at this stage, it is possible that they are interacting with the hydride and this is something under further investigation.

Constantin Sahm said: I noticed that high CO_2 pressures were used during the catalysis. I was wondering why that is and if the catalysts presented here would work under ambient CO_2 pressure as well?

Wendy J. Shaw responded: They do add CO_2 at 1 atm CO_2 and convert it to $HCOO^-$ under stoichiometric conditions. The higher pressures of CO_2 are used to facilitate the rate of catalysis for measurable kinetics in a reasonable timeframe.

Moritz F. Kuehnel asked: Do you think the observed differences between the ethyl and phenyl-containing complexes are to do with changes in the ligand flexibility?

Wendy J. Shaw answered: My expectation is that both ligands would have similar flexibility. However, it is possible that the Ph-substituted ligands would have less access to the active site than the Et-substituted ones. That said, the Ph-substituted complexes had a larger impact from the outer coordination sphere than those that are Et-substituted, so it does not correlate well (or is at least an anti-correlation). It is something to consider, though, as we continue to understand this system.

Leif Hammarström enquired: When decorating catalyst with proton transfer acid/base groups in the secondary sphere to accelerate hydride formation, the assumption is that reprotonation of base is not rate-limiting. We have seen an example in Fe_2 azadithiolate where protonation of the aza nitrogen is much slower than diffusion controlled. Do you have more data on the topic? Do you see any evidence for or against proton transfer limitations?

Wendy J. Shaw answered: While we do not think that is the role of the pendant amine here, with our H_2 oxidation/production $Ni(P_2N_2)^{2+}$ catalysts we definitely saw enhancements with additional proton relays, providing evidence that a single proton relay is not always enough. We think this is due to the hydrophobic groups on the rest of the molecule limiting the transfer of the proton to the solvent. Additional functional groups, such as carboxyl groups, positioned correctly, significantly enhance proton transport into and out of the molecule. This has resulted in lower overpotentials and faster rates.

Shelley D. Minteer remarked: There seems to be an increasing number of researchers using protein enzymes as biological inspiration for catalysts. From a big picture perspective, are researchers also using nucleic acid enzymes (*i.e.* deoxyribozymes) for biological inspiration? It seems as though they are smaller and it is easier to control the outer coordination sphere than in complex proteins.

Wendy J. Shaw responded: Yes, I believe Yi Lu at UIUC is taking this approach. A particular advantage is DNA origami, where DNA can be put in very specific locations. Two disadvantages are the limited number of functional groups compared to proteins and also the sensitivity of DNA to high salts, which would limit their relevance in electrochemical systems.

Souvik Roy queried: Compared to the PNP ligands, how do the $Rh–P_2N_2$ complexes perform towards CO_2 hydrogenation?

Wendy J. Shaw responded: Cliff Kubiak and co-workers evaluated $Rh–P_2N_2$ complexes for CO_2 hydrogenation in ref. 1. He characterized 5 different catalysts. All were active for CO_2 hydrogenation, but were slower than $Rh(depe)_2$ under the conditions used. They suggested that this was due to steric blocking due to the P_2N_2 ligands.

1 A. M. Lilio, M. H. Reineke, C. E. Moore, A. L. Rheingold, M. K. Takase and C. P. Kubiak, *J. Am. Chem. Soc.*, 2015, **137**, 8251.

Souvik Roy asked: Protonation of CO_2 to generate formate seems to be the rate-determining step. Have you tried attaching charged residues to the pendant amines in the second coordination sphere, such as guanidine or imidazolium?

Wendy J. Shaw replied: Yes, we tried to make the arginine (guanidinium group) complex, but were not able to. As a side note, the synthetic challenges we have speak to the earlier question on the synthetic intensity of many of these approaches. We made a Me–His, but had to protect the His due to solubility issues. We did consider making a lysine variant (with a free amine), but there is ample evidence that in the presence of CO_2 this will result in a carbamate. We had less trouble with the Ph-complexes and solubility, so revisiting those complexes with positively charged groups would make sense, although our current plans are to use a structured, model protein and alter the charge within the context of that scaffold.

Daniel Antón-García opened a discussion of the paper by Peter Brueggeller: When you compare the activities of the different metal centers for the chlorido complexes shown in Fig. 4 of your paper (DOI: 10.1039/c8fd00162f), have you checked whether all of the complexes maintain their molecular integrity? Or do they decompose to form nanoparticles capable of hydrogen evolution?

Peter Brueggeller replied: Comparable to the case of Fig. 6 of our paper (DOI: 10.1039/c8fd00162f), where the mercury drop check is depicted in the diagram, this test has also been carried out for the chlorido complexes of Fig. 4. The amount of hydrogen production is the same as that without mercury, indicating that no nanoparticles are responsible for the observed hydrogen evolution. Furthermore, especially for palladium, it has been shown in ref. 1 that only protected nanoparticles lead to reasonable hydrogen production.

1 J. Prock, S. Salzl, K. Ehrmann, W. Viertl, R. Pehn, J. Pann, H. Roithmeyer, M. Bendig, H Kopacka, L, Capozzoli, W. Oberhauser, G. Knör and P. Brüggeller, *ChemPhotoChem*, 2018, **2**, 271.

Daniel Antón-García commented: In the case of the Pt and Co chlorido complexes shown in Fig. 4 of your paper (DOI: 10.1039/c8fd00162f), there seems to be an induction period of 24 h after which the activity increases. How can you explain this if there is no change in the molecular structure of the catalyst?

Peter Brueggeller replied: This can be explained by the exchange of chlorido ligands for solvent molecules. Fig. 6 of our paper (DOI: 10.1039/c8fd00162f) shows that solvato complexes perform better than their chlorido analogues. This exchange is certainly dependent on the kind of metal used. In Fig. 4 the Pt and Co chlorido complexes show an induction period of 24 h, since this is the time needed for the production of the solvato complexes in these cases.

Christine A. Caputo remarked: In your study you extended the PNP ring size, and this had the effect of changing the coordination of the ligand on the metal centre, and ultimately fundamentally changed the mechanism of the catalytic reaction. Have you thought much about this change and how it impacts the results you observed?

Peter Brueggeller responded: Our PNP ligands have been tailored to make different coordination properties possible. Thus for the PNP–C1 ligands coordination of the nitrogen atom is impossible. This makes it feasible for the function as proton relay. By contrast, the nitrogen atom in the PNP–C2 ligands leads to two fused five-membered rings upon coordination. At first glance this should inhibit the proton relay function. However, the catalytic performance of the PNP–C2 ligands is better than that of their PNP–C1 counterparts. DFT calculations show that a different mechanism is responsible for this amazing behaviour, which could be applicable also for other pincer-type ligands.

Moritz F. Kuehnel posed: In your long-term experiments you are continuously adding additional Ir photosensitiser. What are its decomposition products? When you did control experiments, you only used the Ir complex without an HER co-catalyst, and you nevertheless observed some H_2 formation. From my own experience, it is vital to consider that photosensitisers can form HER catalysts not only from their own decomposition products, but also with composition products of the HER catalyst. Have you performed control experiments in which you combined the Ir photosensitiser with *e.g.* only the ligand used for the HER co-catalyst?

Peter Brueggeller responded: It is well known in our laboratory that the Ir photosensitiser alone produces a minor amount of hydrogen as indicated in the paper. For this kind of photosensitiser this is known in the literature. Ir nanoparticles are believed to be responsible for this effect (*e.g.* see M. Beller's work on copper iodide using Ir photosensitisers in ref. 1). However, we have performed amalgam tests in order to study the influence of nanoparticles. Since there was no drop in activity, the observed HER is dominated by molecular species. We did not use Ir as the metal for our PNP catalysts. I agree that this is a good idea to check whether water reducing catalysts (WRC) based on Ir are active catalysts.

1 H. Junge, Z. Codolà, A. Kammer, N. Rockstroh, M. Karnahl, S.-P. Luo, M.-M. Pohl, J. Radnik, S. Gatla, S. Wohlrab, J. Lloret, M. Costas and M. Beller, *J. Mol. Catal. A: Chem.*, 2014, **395**, 449.

Christine A. Caputo said: Going back to the steric effect, there is likely a difference in the functionality of the various groups on your pendant amines and in your paper you attribute this to simply an electronic effect, however you cannot discount the steric effect necessarily. Molly O'Hagan at Pacific Northwest National Lab showed by NMR studies that long alkyl chains on the amines in the P_2N_2 type ligands caused them to move more slowly the bigger the R group (ref. 1). I think this is an important effect that is underappreciated.

1 A. J. P. Cardenas, B. Ginovska, N. Kumar, J. Hou, S. Raugei, M. L. Helm, A. M. Appel, R. M. Bullock and M. O'Hagan, *Angew. Chem., Int. Ed.*, 2016, **55**, 13509.

Peter Brueggeller answered: I agree, this is certainly a so-called stereo-electronic effect as described by P.W.N.M. van Leeuwen. Different R groups change the basicity of the pendant amines and their accessibility for protons due to steric constraints. This has been confirmed by DFT calculations. Slower movement of the protons is of course also a disadvantage. Quite clearly, in our study there is a beneficial effect of small R groups. This important effect has been confirmed in the meantime by preliminary experiments, where R is now H.

Michael Grätzel opened a discussion of the paper by Sergii. I Shylin: Dr Shylin used a sacrificial acceptor, *i.e.* peroxodisulfate, to irreversibly photo-oxidize Ru(II)(bipy)$_3$ to Ru(III)(bipy)$_3$. The latter in turn was used to oxidize water to oxygen using an Fe(IV) complex as a molecular catalyst. I was wondering whether the time resolved laser photolysis experiments revealed any changes in the transient absorption that could be attributed to the conversion of the Fe(IV) to the Fe(V) complex.

Sergii I. Shylin replied: On the microsecond timescale, we observe a negative absorption peak at 650 nm corresponding to the Fe(IV) complex and two positive absorption peaks at 550 nm and 830 nm coming from the Fe(V) complex, seen in Fig. 4b in the paper (DOI: 10.1039/c8fd00167g).

Michael Grätzel remarked: I wonder whether Dr Shylin could propose a mechanism for the formation of oxygen from the reaction of the Fe(V) complex with water.

Sergii I. Shylin answered: The active species should be four-times oxidized to evolve oxygen from two water molecules. The Fe(V) complex characterized in our paper is only a one-electron oxidized species, and we suggest that it is oxidized further. Intermediates beyond Fe(V) appear to be too active, and hence are not observed in the steady-state spectra. Currently we are working on calculations of possible active species involved in oxygen evolution.

James R. Durrant enquired: To drive water oxidation, your catalyst is likely to need to undergo four oxidations. Do you have any evidence that the electron transfer kinetics change with the oxidation state of the catalyst?

Sergii I. Shylin replied: At the moment we know that the overall oxygen evolution undergoes first-order kinetics, and that the initial electron transfer step is a first-order reaction as well. A detailed investigation of the following catalytic steps would certainly provide important additional insights into the reaction kinetics. However, in our flash photolysis experiment we excite only a small amount of photosensitizer and are thus restricted to monitoring the initial hole transfer step. Observation of hole transfer events at the second (or later) step will require quantitative transformation of the catalyst to a desired intermediate prior to the flash, something which has so far proven difficult to achieve.

Sylvestre Bonnet remarked: In Fig. 3 in your paper (DOI: 10.1039/c8fd00167g) you show that photochemical water oxidation works at a constant rate for more than 60 s. In the experimental part you mention an experiment of 140 s. What happens after that time? Do you see the photocatalytic WO stopping? If you do, is the catalyst or the photosensitiser becoming inactive, or both? Did you try adding more photosensitiser or more catalyst to see if photocatalysis would resume?

Sergii I. Shylin responded: Water oxidation stops after 150–240 s. We have found that the iron complex degrades during catalysis due to the decrease in the pH ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). We cannot reactivate water oxidation after these 150–240 s by adding more buffer or base, but the TON can be improved by using more concentrated buffer from the beginning.

Erwin Reisner continued: I have a question regarding the water oxidation mechanism involving the Fe catalyst. You have discussed a possible mechanism for the water oxidation catalysis involving a hepta-coordinate Fe–H_2O species and refer to previously reported Ru-based molecular water oxidation catalysts. However, Ru catalysts such as those reported by Sun and others involve a larger metal ion and a strained equatorial ligand environment, which enables water coordination. The Fe catalyst is well encumbered by the clathrochelate ligand and it is not clear how an aqua ligand would bind. Also, you mention an alternative water oxidation mechanism on the ligand – could you please elaborate on this further and provide more details (maybe also in the context of precedent literature or other evidence)?

Sergii I. Shylin responded: Indeed, the clathrochelate complex discussed in our paper is extremely rigid, so that the formation of the Fe=O oxo-species is questionable unless the integrity of the complex is lost. We are inclined to assume that O–O bond formation may occur on a ligand, whereas the metal center is involved indirectly and facilitates accumulation of holes. A mechanism involving ligand was proposed for the ruthenium “blue dimer” in ref. 1 (see Scheme 4), where an O–O bond is formed on carbon as a fragment of the four-membered endoperoxide ring, C_2O_2. We acknowledge that the mechanism of water oxidation using the clathrochelate complex remains elusive and is not discussed in our paper. Currently we are working on the modification of clathrochelate ligands in order to stabilize the active species (to make it ‘less active’). In parallel, calculation studies of the supposed intermediates are ongoing.

1 J. K. Hurst, J. L. Cape, A. E. Clark, S. Das and C. Qin, *Inorg. Chem.*, 2008, **47**, 1753.

Christine A. Caputo enquired: At the end of your manuscript you suggest that you could modify the ligand by adding a methyl group, and hypothesized that this would provide the complex with more stability. Is the synthetic approach to making the proposed methylated molecule quite straightforward?

Sergii I. Shylin replied: The iron(IV) clathrochelate complex spontaneously assembles in aqueous media from low-valent iron salts, oxalodihydrazide and formaldehyde in the presence of atmospheric oxygen. It is a simple one-pot template reaction that can be reproduced even in a minimally equipped school laboratory. The use of other aldehydes instead of formaldehyde would lead to modified clathrochelates, *e.g.* starting from iron(III), oxalodihydrazide and acetaldehyde, the methylated complex can be obtained.

Christine A. Caputo addressed a question to Wendy J. Shaw, Peter Brueggeller and Sergii I. Shylin: In many of these papers, the structure activity relationships rely on the synthesis of a library of ligands and complexes, which is a significant effort and often the synthetic modification is quite challenging. My question to the panel is: is the approach and the synthetic effort worth the payoff?

Peter Brueggeller responded: In this context it is worthwhile to learn from nature also with respect to coordination chemistry. Nature has invented porphyrin ligands during evolution. From a preparative point of view these ligands would be very expensive when produced by chemists. On the other hand these ligands combine chelate and macrocyclic effects, which are absolutely necessary for the complexation of metals like magnesium. Also, for artificial photosynthesis one can postulate a simple rule: inexpensive metals like 3d metals lead to a more difficult coordination chemistry and there is the need for sophisticated ligands. Since at the end the costs for a whole artificial device count, the synthetic effort is worth the payoff, especially when earth-abundant metals come into play.

Wendy J. Shaw replied: Yes. In order to get to a more sustainable future, we need to be able to develop better catalysts. From everything we know, the best way to do this is to mimic features of enzymes, not necessarily structurally but functionally. This requires good synthetic capabilities to test the proposed principles. For an ultimate application, the synthesis will need to be scalable, high yield and reasonably straight forward, but getting to a solution will require many syntheses, including homogeneous, heterogeneous, and biological. Investing in synthetic capabilities is essential to develop the catalysts we need to answer the fundamental questions we have.

Leif Hammarström commented: Regarding photocatalytic water oxidation or hydrogen production, where the rate of gas evolution is plotted as a function of the irradiation time, the observed rate does not directly reflect the rate of any catalyst steps. Instead, it is equal to the rate of photon absorption times the quantum yield for product formation. Quantum yields are typically low, so most of the reaction is recombination or side reactions. Thus, a comparison of rates between different systems does not necessarily give information on the rate of the catalytic steps.

Peter Brueggeller responded: In our photocatalytic HER experiments the Ir photosensitiser was clearly the less stable species, when compared with the WRC. However, the photosensitiser alone produces very poor HER results. This means that side reactions involving the photosensitisers can be neglected. Also the production of reactive nanoparticles has been ruled out by amalgam tests, thus excluding also these side reactions. Furthermore, we have studied a whole series of WRC, where only the metals differ in otherwise identical systems. So why not make the different metals used responsible for the observed HER? The proposed different catalytic cycles for the PNP–C1 and PNP–C2 ligands are confirmed by DFT calculations. However, I agree that these cycles are related to the forward reactions and indeed recombination reactions could also differ.

Sergii I. Shylin responded: I agree with your comment. In our photocatalytic experiments, we used excess amounts of photosensitizer $[Ru(bpy)_3]^{2+}$. Hence, we assumed that the overall performance of the photocatalytic system was determined by the catalyst. In addition, we investigated the kinetics of water oxidation using the one-electron oxidant $[Ru(bpy)_3]^{3+}$ (prepared separately) in darkness. In both the photochemical and chemical experiments, the initial rates of oxygen evolution exhibited a linear dependence on the catalyst concentration.

Michael Grätzel continued: As a follow up of Prof. Hammarström's question, the point is that the $[Ru(bpy)_3]^{3+}$ may not have a high enough redox potential to drive the oxidation of Fe(v) to Fe(vi) On the other hand the peroxosulfate anion radical formed as an intermediate from the one electron reduction of peroxodisulfate does have a high enough redox potential to drive this reaction. To rule out this possibility one would have to use a one electron oxidant such as Ce(iv) to affect the water oxidation.

Sergii I. Shylin replied: That is true. We cannot completely exclude the impact of the sulfate radical on oxygen evolution in photochemical water oxidation. However, we have shown that $[Ru(bpy)_3]^{3+}$ prepared separately does evolve oxygen from water when added to the Fe(iv) catalyst. Hence, $[Ru(bpy)_3]^{3+}$ is able to oxidize the catalyst beyond Fe(v). Alternatively, we could use ceric ammonium nitrate, but it would have required an acidic pH, something which we would like to avoid.

Anastasia Vogel directed a question to Wendy J. Shaw: Considering the interaction of the outer coordination sphere with both the active centre as well as the solvent, do you expect to see a solvent effect on the series of presented TONs/TOFs? If so, may there be an optimum pairing of solvent and outer coordination sphere residues?

Wendy J. Shaw responded: Within a given solvent, I expect to see limited solvent effects. The solvent primarily affects the hydricity, so comparisons between solvent are the most meaningful. It is possible that as we go to a larger protein structure, the protein effectively shields the solvent in different ways, resulting in an effective solvent effect, but I would attribute this more to the scaffold than to the solvent. There is likely an optimum combination of solvent effects and scaffold effects, but ultimately I believe that being able to precisely control where particular atoms are, solvent or scaffold, will yield the best catalysts.

Anastasia Vogel continued: Following up on the previous question, would you expect such a solvent effect on TONs/TOFs due to the interaction with the outer coordination sphere to be larger than other changes (*e.g.* changed mass transport due to different polarities of solvents)?

Wendy J. Shaw responded: I think there is that possibility. In the end, the rate-determining step for any given reaction will dictate what effects the solvent and the scaffold have. In this case, within a given solvent, there is no evidence of an overriding impact beyond controlling the hydricity.

Joost N. H. Reek asked: I really like your approach of controlling reactivity using the second coordination sphere, installing functional groups that are also playing important roles in enzyme cavities. Looking at the mechanism that you propose it seems that the CO_2 activation (step 3) is RDS. (1) Do you have more detailed insight into how this CO_2 activation occurs?

(2) Mark Roberts demonstrates with his porphyrin based catalyst that the secondary interaction with CO_2 is important. In the CO_2 activation step, negative charge accumulates on oxygen which means that cations or hydrogen bonds may stabilise the TS and thus speed up this reaction. You have not included such functional groups in your library. Have you considered functional groups that have hydrogen donors? Simple amine bonds may be sufficient.

Wendy J. Shaw answered: Yes we considered amines, but due to the formation of carbamates, we have not pursued it. The Me–His system is not charged and we were unable to synthesize the arginine system. It is a great thought though and one we are now pursuing in the context of a structured protein scaffold. Regarding the CO_2 addition for the Ph complexes, previous work by Linehan *et al.* in ref. 1 using a Co metal center calculated either a mechanism in which CO_2 bound, or one in which the CO_2 reacted directly with the hydride. The results were within a few kcal mol^{-1}, so either option for the mechanism could be equally likely. We were hoping that the Rh system would provide more distinction. Unfortunately, with the Et complexes, extensive computational DFT studies do not provide agreement with the experimental studies, specifically the deprotonation step appears to be much easier in the calculations than is observed experimentally. We are continuing to apply more advance computational studies to address this, but at this stage, we do not have a definitive answer on the mechanism.

1 M. S. Jeletic, M. T. Mock, A. M. Appel and J. C. Linehan, *J. Am. Chem. Soc.*, 2013, **135**, 11533.

Joost N. H. Reek remarked: The ligands that you use have a lot of flexibility which could potentially lead to different conformations of these ligands around the metal center. It could be that the functional groups that you install on your ligands may influence the distribution of conformations How can you distinguish between real secondary sphere effects and an indirect effect in which the functional groups just changes the ligands conformations? Could phosphorus NMR be of any help?

Wendy J. Shaw answered: Great observation – there is no doubt that the PNP ligands are moving relative to the metal center. This is further supported by ample studies on the P_2N_2 ligands which do show structural restriction. We do not see any difference by ^{31}P-NMR and have done many low temperature experiments to investigate this. While we do not see any direct correlation with mobility, even in the P_2N_2 rings which are much more motionally restricted, it is still difficult to create interactions which slow these motions. This can be done with groups that can interact with each other (aryl rings, or very long chains which can slow chair-to-boat interconversions). In this case we don't have anything large enough to slow these interconversions. The aryl rings could potentially interact to lower the PNP mobility, but there is no evidence that this is correlated to the TOF. It is worth considering, and within the protein scaffold we are moving to we should be more able to evaluate the mobility of these ligands.

Christine A. Caputo addressed Sergii I. Shylin, Peter Brueggeller and Wendy J. Shaw: All of the panelists have utilized some rare and precious metals in their photocatalytic systems. The impetus, of course, is that we move towards systems with more abundant metals for sustainability purposes. Could all of the panelists comment on their choice of metal used in their catalytic system?

Sergii I. Shylin responded: Water oxidation systems consist of several components: an oxygen-evolving catalyst, photosensitizer, electron acceptor, *etc.* Thus, there are so many variables which influence the overall performance of the catalytic system. If we investigate the water oxidation part of the system (indeed it is based on iron, the most abundant transition metal), we need to use the efficient photosensitizer $[Ru(bpy)_3]^{2+}$ with known properties. We could use a noble metal-free light harvester, but our system would be limited by its efficiency. When an efficient catalyst is found and characterized, one can use it in a system to screen potential photosensitizers based on abundant elements. When catalyst and photosensitizer are found, one can vary the third component, and so forth.

Peter Brueggeller answered: Since the main focus of our paper concerning the ligands is on phosphines, it is interesting to note how these ligands change their coordination properties as soon as different metals are involved, *e.g.* using the expensive metal osmium produces chromophores which are stable for more than six weeks (see ref. 1). This is not possible for inexpensive 3d elements like nickel, which is certainly a consequence of the HSAB principle. The same considerations are also valid for WRCs: 3d elements usually show a more complicated coordination chemistry leading to less stable complexes than their more expensive 4d and 5d counterparts.

1 J. Prock, S. Salzl, K. Ehrmann, W. Viertl, R. Pehn, J. Pann, H. Roithmeter, M. Bendig, H. Kopacka, L. Capozzoli, W. Oberhauser, G. Knör and P. Brüggeller, *ChemPhotoChem*, 2018, **2**, 271.

Wendy J. Shaw replied: In our case, we are focused on understanding how the outer coordination sphere works. In order to do this we need a well understood core catalyst and a good attachment point for the outer coordination sphere. The $Rh(PNP)_2$ system provided that. There is a similar system with Co that is also very well understood, unfortunately, it does not have a place to attach a protein to create a scaffold so it would not work to answer the questions we are interested in answering. In principle, the design principles we are developing should be extended to other metals and systems, so we do not see the use of a precious metal as limiting in this respect.

Matthias Beller commented: It is not so important for these examples to move from noble to non-metal, the next step is to move to more integrated devices – it is more important to be using and implementing in real devices. This is interesting for organometallic chemistry but needs to be applied for artificial photosynthesis.

Peter Brueggeller responded: I agree that it is a difficult task to think of real economically possible devices for artificial photosynthesis. However, in my opinion, using environmentally benign and inexpensive metals is an important step towards an affordable device. Of course there are other factors, *e.g.* the TON: a TON of about one million would certainly allow also noble metals, which can be recycled at least in principle.

Another point is of course the sacrificial donor. Nature uses water and this should also be the goal for artificial systems. One has to keep in mind that the hitherto most efficient systems like Nocera's artificial leaf are very expensive, in part also because of the membrane containing palladium. Another highly efficient device is certainly Eisenberg's system using cadmium chalcogenides in the form of quantum dots for the chromophores (ref. 1). Cadmium chalcogenides are so poisonous that they are forbidden within the European Union.

1 Z. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, *Science*, 2012, **338**, 1321.

Simon T. Clausing then said: Systems for photocatalytic water splitting are often optimized towards their pH value. However, this is usually always the optimization towards a compromise: the sacrificial electron donor (for the water reduction side reaction) functions optimally at a high pH value, and the catalyst might be active at a far lower value, so the full system lies somewhere in between. Ultimately, however, the community wants to leave behind the dependence on sacrificial donors and acceptors. Would it therefore not be sensible to try and find a way to optimize the optimal conditions for only the catalyst, and not a combined catalyst-and-donor system? Have any of you thought of approaches to achieve this goal?

Peter Brueggeller responded: It is true that in sacrificial systems the pH dependence may mainly reflect the pH dependence of the sacrificial donor used. Usually a lower pH is an advantage, since more protons are present. However, it is known in the literature that sacrificial donors like triethylamine show better reduction potential in more basic solutions. Hence, the result is a maximum usually in the range of pH 9–10. So the solution to this problem is of course the independence of sacrificial donors. One possibility is to deliver the electrons electrochemically. The second is to construct so-called combined systems where, as in nature, water is used as the electron donor.

Sergii I. Shylin replied: It is absolutely possible in a photoelectrochemical experiment, with an electric current as the 'pH-independent electron donor'.

David Wakerley asked Sergii I. Shylin: Can you provide evidence on your CV to confirm that the catalytic oxidation wave is O_2 formation and not the oxidation of your ligand?

Sergii I. Shylin replied: We have found using UV–Vis spectroscopy that the complex remains stable after 2 h of bulk electrolysis at 1.4 V *versus* NHE. The spectra of the solution under study taken before and after electrolysis are identical. In addition, in our CV the peak current is linearly dependent on the square root of the scan rate that indicates a homogeneous process in solution, but not on the electrode surface. So the impact of possible decomposition products, such as oxides, on the catalytic current is ruled out.

Han Sen Soo commented: In Fig. 4a of your manuscript (DOI: 10.1039/c8fd00167g), I noticed that the spectra were assigned to $[Ru(bpy)_3]^{2+*}$, but the spectral features are not fully consistent. In the transient absorption spectrum of the Ru* excited state, there is usually both a groundstate bleach as well as the emission spectrum. However, even at very short time scales of 20 ns, the emission component around 600 nm is already absent. I believe that these bands should probably be assigned to the Ru(III) instead.

Joost N. H. Reek enquired: In your conclusion you mention that this catalyst gives the fastest hole scavenging when combined with the ruthenium chromophore, and this is proposed to be important for the stability of the chromophore. Do you understand why this particular complex leads to fast hole scavenging, and could this lead to design criteria for future catalyst development?

Sergii I. Shylin answered: The robust nature of the clathrochelate ligand provides the catalyst with additional stability. Thus the catalyst is able to re-reduce $[Ru(bpy)_3]^{3+}$ repeatedly without degradation. Currently we are working on the modification of the ligand in order to improve its stability.

Joost N. H. Reek continued: So you conclude that it is only a matter of stability of the catalyst?

Sergii I. Shylin responded: It is an important factor, but not the only one. We should also consider thermodynamics, specifically the accessibility of the Ru^{III}/Ru^{II} redox couple by the catalyst.

Christine A. Caputo addressed Peter Brueggeller, Wendy J. Shaw and Sergii I. Shylin: Thinking about structure activity relationships, did any of the panelists use a significant amount of computational chemistry in the design of your molecular systems?

Peter Brueggeller responded: I agree that computationally predicting the best catalysts is still difficult. However, in our case DFT calculations show that during charge transfer and reduction of the WRC the metals seem to become too electron rich in the presence of anionic chlorido ligands. So the calculations predicted that the chlorido ligands are expelled from the coordination sphere as soon as the metals in the precatalysts are reduced. As a consequence we decided to already remove the chlorides from the precatalysts and use solvato complexes. Indeed the catalytic performance of the solvato complexes outperforms that of the corresponding chlorido complexes. This has also practical consequences: the use of salty sea water can be detrimental for the hydrogen evolution reaction.

Wendy J. Shaw responded: We work very closely with computational chemists in all aspects of our work. Unfortunately, computationally predicting the best catalysts is still difficult. There are places they can contribute very well at this stage, for instance, we are using MD to determine the amino acid mutations we should make to control catalysis with a protein-based scaffold. Further understanding how the catalysts work will get us closer to computationally-designed catalysts.

Qian Wang opened a discussion of the paper by Wilson A. Smith: I am curious about the stability of the copper borate oxide layer. Have you checked the sample using XPS after a long-term test?

Wilson A. Smith replied: The stability is based on the operation time and applied potential. If the photocharged sample is held at a constant potential (and under illumination), the current will slowly decrease over time and revert back to the value of the pure $CuWO_4$ electrode. We haven't checked XPS after long term measurements, but we assume the decrease in photocurrent is due to the degradation of the borate layer.

Qian Wang asked: You mentioned that several materials exhibited the same effect. However, different materials have different band structures. I was wondering how you confirm that the formed oxide layer will show suitable band structure matching that of the semiconductor as expected.

Wilson A. Smith responded: It has been shown here that in a borate electrolyte, the $CuWO_4$ photoanode forms a large band gap metal oxide on the surface. Similarly, for the $BiVO_4$ photoanode in a borate electrolyte, a large band gap metal oxide made from borate forms on the surface, and for the BiVO4 photoanode in a phosphate electrolyte, a large band gap metal oxide made from phosphate forms on the surface. It happens that in these cases, metal oxides made with borate and phosphate have larger band gaps than those of $BiVO_4$ and $CuWO_4$ (and many of these materials exhibit glass-like properties). Therefore it happens that borate and phosphate electrolytes form borate- and phosphate-containing metal oxides which have larger band gaps than photoactive metal oxides, leading to beneficial charge separation/catalysis.

Andrew B. Bocarsly asked: You spoke about a chemisorbed species as the top layer of the junction, but you also spoke about it being ~5 nm thick. This is too thick to be a chemisorbed layer. It is either approximately a monolayer or it is a thin film (~5 nm). What picture does your data support?

Wilson A. Smith replied: We believe that the layer really is only chemisorbed, and only mention that the layer is ~5 nm thick because this is the penetration depth of the XPS. Since we still see the signal from the underlying $CuWO_4$ layer we do not think that the layer is complete or as thick as 5 nm.

Virgil Andrei queried: Why are open-circuit conditions required to form the heterojunction? Would the copper borate surface layer form faster when applying a slightly positive or negative potential during irradiation? Under those conditions, no photoelectrochemical oxygen evolution should occur; therefore, any small currents may be traced back to changes in the surface composition.

Wilson A. Smith answered: We have shown that applying a potential close to the photovoltage of the electrode, and for over 20 h in the dark, also promotes an improvement in the photoelectrochemical performance. However, the improvement is much smaller than that during the photo-induced process. This may be because of differences in charge carrier density, diffusion within the bulk of the material, and quasi-fermi level splitting during photon-induced photocharging, which favors passivation of surface states close to the illuminated surface.

Virgil Andrei asked: The paper mentions that copper borates are proven photocatalysts. However, this layer can account for very little light absorption due to its thickness of only 5 nm. In this case, can it really be considered a photocatalyst, or does it act more as a passivating layer/electrocatalyst?

Wilson A. Smith responded: After finding that we most likely had a copper borate layer on our surface, we looked into the literature and saw that this material has recently been shown to have photocatalytic properties. Since the copper borate layer found on top of our $CuWO_4$ electrode was so thin, we do not believe it contributed to the light absorption and photocatalysis. Therefore, our comment about copper borate being a photocatalyst was from its previous use in the literature and not its activity in our work. For our paper, we believe that it indeed acted as a passivating layer and potentially as an electrocatalyst.

Charles E. Creissen requested: Can you comment on the use of methanol as a hole scavenger and its ability to distinguish between the bulk and surface properties of the semiconductor?

Wilson A. Smith replied: We used methanol as a hole scavenger for reasons of stability and enhanced oxidative performance. In the literature, it is typical to use methanol, hydrogen peroxide, or $NaSO_4$, and here we chose methanol because it worked best with the $CuWO_4$ photoelectrode we use, while we use H_2O_2 for other materials such as $BiVO_4$.

The use of a sacrificial agent should be used to correlate current/voltage characteristics with and without this reactant, which can then provide information about catalytic and charge separation efficiency. The idea is that a sacrificial agent has a ‘maximum’ catalytic activity for a given material, so when the same electrode performs water oxidation without it, we can see how close/far from this ‘maximum’ behavior it is. Likewise, by including the incident photon flux and optoelectronic properties of the material (*i.e.* band gap), we can also roughly estimate the charge separation efficiency.

Charles E. Creissen enquired: How does the degree of surface hydroxylation influence catalysis especially, considering the role of hydroxyl radicals in MeOH oxidation?

Wilson A. Smith answered: We find that surface hydroxylation improves catalysis, and occurs spontaneously in the dark when a (metal oxide) photoelectrode is placed in an electrolyte. After soaking in the electrolyte, and increasing hydroxylation (measured in a separate work by operando X-ray Raman spectroscopy), the PEC performance improves. For the case of MeOH oxidation, this was used as a sacrificial oxidative reaction that should occur more easily than water oxidation, and indeed we see high photocurrents and lower onset potentials for this reaction.

James R. Durrant commented: Your talk gave some very interesting insights. Could you comment on what you mean by the term ‘photocharging’? I note that in your figure illustrating photoanode function, your ‘photocharged’ photoanode is not drawn with more charge.

Wilson A. Smith answered: The term photocharging is indeed somewhat of a misnomer. Many years ago when we first discovered the phenomenon using $BiVO_4$, the PhD student at the time (now Dr Bartek Trzesniewksi), thought the enhanced performance looked like the system had been charged like a battery, and hence called it ’photocharging’. The name does not mean that there is excess charge on the surface (though the surface chemistry does change), so I/we understand that the name is not ideal and may be somewhat misleading if taken literally. We will try to re-name the phenomenon in subsequent work.

James R. Durrant continued: I note that in your electrode energy level diagram the copper borate valence band is deeper than that of copper tungstate. Could you comment on how water oxidation proceeds on this electrode, and particularly where photogenerated holes accumulate to drive this reaction?

Wilson A. Smith answered: The band diagram was drawn for illustrative purposes, and is by no means exact. First, the layer of copper borate is less than 5 nm, and thus may not be thick enough to form an appreciable layer that has a large enough density of states to make a formal or well-defined band structure. In addition, there are 2 structural forms of copper borate (CuB_2O_4 and $Cu_3B_2O_6$) with 2 different band gaps (3.1 eV and 2.16 eV). Due to the non-qualitative nature of the XPS results that showed a change of Cu valence, and an increase in a unique O feature and B peak, we cannot definitively say which composition of copper borate we found. As we did not see an appreciable change in the band gap or band edge, we made the implicit assumption for this diagram that the larger band gap copper borate was there, leading to the figure as drawn. We also saw evidence of enhanced charge separation, which is more likely with a hetero-junction with a large band gap material compared to that with a smaller band gap material. Our illustration was not meant to be qualitative, and is only schematic to show the materials properties change we measured (0.4 eV shift in Fermi level), improved catalysis/charge separation, and new Cu/O/B signals from the surface.

Putting this all together, we believe that photogenerated holes in $CuWO_4$ may tunnel through the very thin layer of copper borate, where this layer only provides enhanced charge separation in the space charge region, which may also aid in hole accumulation compared to the bare $CuWO_4$/electrolyte interface.

Chanon Pornrungroj remarked: Could you elaborate more on the comment you made about the day–night cycle (charge/discharge) of the $CuWO_4$ layer and how it would affect the long-term stability of this material?

Wilson A. Smith replied: We observe that the process of the surface hetero-junction forming occurs during illumination, and is removed when the light is turned off. Therefore, in a practical system that turns on and off every day when the sun goes up and down, the surface oxide layer will form, dissolve, and re-form every single day. If the removal of the layer removes Cu or W from the electrode, then each cycle will physically degrade the electrode and over time will remove all of the photoactive material. Therefore, although the photocharging technique brings significant improvement in photoelectrochemical performance, its practical utilization could be hindered by catalyst dissolution in the dark.

Michael Grätzel asked: The hole currents you observed upon polarizing the copper tungstate look like capacitive charging currents and not Faradaic currents. My question is where do the electrons go ?

Wilson A. Smith replied: This is a great question, and it seems this may be different for every material that can photocharge. We see from XPS that the surface valence of Cu changes, but there is a reduction in the Cu^+ peak, which correlates to the oxidation of Cu by anionic adsorption. So far, we cannot account for the photogenerated electrons, but it may relate to bulk defect chemistry which we hope to probe in the coming years.

Andrew B. Bocarsly noted: It is well established that polycrystalline electrodes yield a poorer current–potential and quantum yield response than that observed with single crystal electrodes. This is often attributed to grain boundaries acting as recombination sites. Could grain boundary processes be added to your simulation? Is it possible that the surface layer you are forming is occurring primarily at grain boundaries? If so, how will this impact the expected I–V response?

Wilson A. Smith responded: This is a great question, and one that we share and have already started to address internally. We plan on using *in situ*/operando electrochemical atomic force microscopy (EC-AFM) to observe the surface of our photoelectrodes during operation, and map the current density distribution spatially over the electrode surface. This should allow us to see where certain ’hot-spots’ are for activity, and if indeed they occur at grain boundaries or along edges/planes/corners.

Michael Grätzel commented: Many researchers are looking for new metal oxide materials. What is promising about your tungsten materials ?

Wilson A. Smith responded: The $CuWO_4$ photoanode we study has a slightly smaller band gap than $BiVO_4$, but after a few years of research it seems that its optoelectronic and catalytic properties cannot be improved like $BiVO_4$ despite efforts of doping, surface passivation and the use of co-catalysts. I think this brings up an important point in the search for ’winning’ materials in the field of photoelectrochemistry. Even if a new metal oxide photoelectrode can convert all of the incident sunlight to electrical/chemical energy, I have serious doubts about the scalability of this approach to scale up to meet TW, GW or even MW needs. Efforts should instead focus on understanding mass transport, reactor engineering, and scaling up of this technology, which need to be solved in parallel to materials optimization.

Ravi Shankar added: Following on from Professor Grätzel’s comment, what do you think the key limitations are for solar fuel production through photoelectrochemistry? Do you envision some sort of feedback loop?

Wilson A. Smith answered: I think the key limitations for solar fuel production through photoelectrochemistry (PEC) are predominantly engineering: mass transport, reactor engineering, process intensification, process integration, *etc.* The field has been focused on materials properties for four decades, and we are still not in a place close to commercialization or industrial applications. While we do still need to find photo and electrocatalysts to perform key redox reactions (with low overpotential, high stability and high selectivity), we need a massive increase in the areas that look to apply these materials in practical systems. For example, we need to already think: what if we find an 'ideal' material that meets all of the metrics we pose on PEC? Then what? We need to already be thinking about this now, so that when in the next years or decades we do find these materials, we can already put them in a place to upscale.

We cannot wait to find the 'ideal' material, then worry about making the process at the MW, GW or TW scale. In addition, from other fields where large scale electrolysis is performed, it may turn out that the process conditions needed for practical applications are far removed from where a majority of lab-scale testing is done. That means that we may be optimizing the performance and understanding of materials and processes in a regime that is not industrially relevant. Therefore, we absolutely need a positive feedback loop between engineers and materials scientists/chemists to understand what a large scale system may look like in order to give us more realistic conditions to improve materials and systems in a laboratory scale, that can have a faster pathway towards industrial applications.

Sergii I. Shylin enquired: You suggest that formation of a copper borate complex at the electrode surface after the photocharging treatment may contribute to the improved performance of $CuWO_4$. As such, would it be possible to dope the surface of $CuWO_4$ with borate by other methods than light irradiation (*e.g.*, by refluxing electrodes in sodium tetraborate solution)?

Wilson A. Smith responded: This is possible, but we have not tried it. As long as there are borate anionic species in the electrolyte and electronic defects at the surface, there could be spontaneous adsorption, but it may not be energetically favorable to occur at all, or may be very slow (and the photoinduced process we show may simply speed up the reaction.).

Andreas Wagner questioned: Is this effect similar/comparable to work published by Michael J. Rose and co-workers in ref. 1? They show covalent molecular functionalisation of silicon semiconductor surfaces to influence surface recombination and carrier density.

1 D. G. Boucher, J. R. Speller, R. Han, F. E. Osterloh and M. J. Rose, *ACS Appl. Energy Mater.*, 2019, **2**, 66.

Wilson A. Smith replied: I think these works are very similar in that anionic adsorption passivates defects at the SLJ. In the case of silicon, dangling bonds or defects in a surface SiO_x layer make preferential adsorption of different molecules, and in our case the anionic borate and phosphate species adsorb to surface defects. In our case the defects are not as clearly characterized, but are most likely related to oxygen vacancies or Cu with non-ideal valence. We are going to probe these surfaces *in situ*/operando with FTIR to see if we can observe which surface species form as a function of potential/electrolyte.

Martijn A. Zwijnenburg asked: This is perhaps a naive question, but would a photoelectrode in a water splitting photoelectrochemical cell routinely be illuminated under open circuit conditions? If not, would photocharging ever occur for such a cell?

Wilson A. Smith replied: That is a great question. For a 'practical' cell, there would need to be at least 2 photoactive materials, as significant modelling work has shown that the best approach to get a high solar-to-hydrogen conversion efficiency is with a tandem absorber configuration. Therefore, if a metal oxide is the top layer, *i.e.* interfacing with the electrolyte, it would always receive a voltage boost from the bottom absorbing material, which would indeed not be true open circuit conditions. However, in the literature it has been shown that photocharging with an applied potential can make the process go even faster, so this may benefit an overall device system.

Ravi Shankar opened a discussion of the paper by Aubrey R. Paris: Aubrey, in Fig. 6 of your paper (DOI: 10.1039/c8fd00177d) you show the different Faradaic efficiencies for your different materials. Could you comment on the influence of the support that you use in your materials as it appears that this seems to have an effect?

Aubrey R. Paris answered: We initially showed that the choice of solid support can influence catalytic activity, specifically for the Ni_3Ga intermetallic, in ref. 1. Following thorough materials characterization, we suggested that the differences in catalytic activity (including product distribution) observed for this species on different carbons could be attributed to changes in surface composition and morphology. In the report prepared for this Faraday Discussion, we decided to probe the carbon support dependence further. The most interesting result of these experiments was the fact that carbon solid supports could not reinstate multi-carbon generation ability for non-intermetallic Ni–Ga films. This result supports our 2018 report, which does not attribute a direct role to the carbon in influencing catalytic behavior (rather, its effect is indirect in dictating the composition and morphology of the surface during catalyst synthesis). However, a consistent point of interest in our 2018 paper and the study presented here is the fact that thin films deposited on glassy carbon and reticulated vitreous carbon (RVC), which are structurally similar materials, generate the same products from CO_2 but in different Faradaic efficiencies. Specifically, RVC-grown films exhibit approximately double the Faradaic efficiency for each carbon-containing product compared to those on glassy carbon. This is unexpected, because the greater surface area of RVC films should not intuitively result in greater Faradaic efficiencies (if anything, a greater current density would be expected). We have yet to understand the chemical reasoning for this observation.

[1] A. R. Paris, A. T. Chu, C. B. O'Brien, J. J. Frick, S. A. Francis and A. B. Bocarsly, *J. Electrochem. Soc.*, 2018, **165**, 385.

Ravi Shankar noted: Aubrey, you mentioned in your paper that you presume the CO reduction to be rate-limiting step and that this goes against your previous work. Could you please explain a bit more about this?

Aubrey R. Paris replied: Based on the results of the D_2O electrolyte experiments, it is likely that CO reduction is rate-limiting. However, I should caution that whether or not this is true depends on why the D_2O is affecting the system as it is. For example, if the D_2O is simply slowing down the reaction pathway that is active in H_2O-based electrolyte, then CO reduction should be rate-limiting, but this would not necessarily be the case if the presence of D_2O activates a different catalytic pathway for the system.

In our initial report about the multi-carbon product generation ability of intermetallic Ni_3Al (ref. 1) we used the rate of liquid product formation to hypothesize the rate-determining step of CO_2 electroreduction. In essence, we found that supplying the system with CO feedstock instead of CO_2 resulted in faster product generation, so we suggested that CO_2 reduction to CO might be rate-limiting. Based on the D_2O experiments described in this work, however, that may not actually be the case. A more thorough understanding of the nature of D_2O's effect would likely help discriminate between these two rate-limiting step possibilities.

1 A. R. Paris and A. B. Bocarsly, *ACS Catal.*, 2017, **7**, 6815.

Andreas Wagner asked: Why did you choose to use pH 4.5 sulfate (+bicarbonate) electrolyte, given that pure bicarbonate buffers are much more widely used in CO_2 electrocatalysis? Was the buffer used in the D_2O experiments also prepared in the same manner?

Aubrey R. Paris responded: While bicarbonate buffers are certainly common in this field, they more easily facilitate electrochemical experimentation in the pH 6.8–7.2 range. However, we have shown previously that pH 4.5 is optimal for the parent intermetallic films discussed here, which we presume is due to the high solubility of CO_2 in water at this condition. This actually tends to be the optimal condition for many of the heterogeneous CO_2 reduction catalysts studied in our lab, frequently resulting in our selection of K_2SO_4 as an electrolyte, because it requires a very small amount of $KHCO_3$ to achieve a buffered solution close to pH 4.5. We also often select K_2SO_4 for our electrolyte because we perform pH dependence studies with any new catalyst we develop, and the $K_2SO_4/KHCO_3$ combination allows for examination of a wide pH range (approximately 3.5–7.5). Experiments using D_2O were indeed prepared in the same manner.

Wendy J. Shaw queried: You stated that the role to make multiple carbon chains is indirect. Can you provide any more comments or speculation on this mechanism?

Aubrey R. Paris responded: I would not call the mechanism indirect, but rather the experiments we used to begin probing it were indirect indicators of what it may or may not look like. At this point, we seem to understand that generating multi-carbon chains on these nickel–Group 13 metals is predicated on intermetallic character, suggesting that the role of the two metals is synergistic, or electronic, in nature. This does not rule out the possibility that the two metals on the surface could also provide distinct binding sites to further stabilize CO_2 or the reduction intermediates, but our experiments here do indicate that this "co-stabilization" effect is not the sole reason for multi-carbon product generation. The next steps in further understanding the reduction mechanism should definitely focus on interpreting the H_2O/D_2O effect. Because it is possible to imagine many reasons for this unexpected effect, experiments ruling out certain reasons would be extremely informative. These experiments could include *in situ* studies to examine differences in surface-bound reduction intermediates in the presence of H_2O *versus* D_2O. Importantly, because we have now observed this effect in four different CO_2 reduction systems (*i.e.*, the two discussed here, plus our recent report on a Cr–Ga oxide alloy and another unpublished catalyst from our lab), it seems to be at least a somewhat conserved effect. Understanding it could tell us a lot about CO_2 electroreduction systems as a whole.

Wilson A. Smith commented: The idea of bimetallic or alloy catalysts is interesting from the perspective of changing selectivity according to the composition of active sites for different reactions. However, when you apply the same potential to different metals, not only do they have different selectivities, but they also may have different current densities. What are your thoughts about the activity/current density distribution for bimetallic or alloy catalysts, and how differences in activity on different metallic sites can affect overall selectivity and mechanistic understanding?

Aubrey R. Paris replied: You raise a really important point regarding the design of these electrocatalytic systems. Eliciting two specific reduction events on two distinct surfaces (in the same electrochemical cell) requires compatible electrochemical conditions for the two surfaces, such as an optimized operating potential, pH, and electrolyte salt. This is why I note in the conclusion section of the paper that a single alloy or intermetallic species should theoretically be easier to optimize than coupling two distinct electrodes performing complementary tasks. Nonetheless, this complication does not negate the mechanistic assertions made in the paper, because the product distributions achieved using the "striped" or non-alloyed electrodes seem to be combinations of the product distributions found using single-metal controls.

Sarah Lamaison asked: Some recent articles in the field[1–4] propose to use the binding energies of the reaction intermediates on the individual metals as descriptors to rationalise the selectivity of these alloyed metals. Have you tried to look into that? And if so, are the experimental data consistent with such rationalisation?

[1] T. Hatsukade, K. P. Kuhl, E. R. Cave, D. N. Abram, J. T. Feaster, A. L. Jongerius, C. Hahn and T. F. Jaramillo, *Energy Technol.*, 2017, **5**, 955.
[2] S. Lamaison, D. Wakerley, D. Montero, G. Rousse, D. Taverna, D. Giaume, D. Mercier, J. Blanchard, H. N. Tran, M. Fontecave and V. Mougel, *ChemSusChem*, 2019, **12**, 511.
[3] A. Bagger, W. Ju, A. S. Varela, P. Strasser and J. Rossmeisl, *ChemPhysChem*, 2017, **18**, 3266.
[4] Y. C. Li, Z. Wang, T. Tuan, D. –H. Nam, M. Luo, J. Wicks, B. Chen, J. Li, F. Li, F. Pelayo García de Arquer, Y. Wang, C. –T. Dinh, O. Voznyy, D. Sinton and E. H. Sargent, *J. Am. Chem. Soc.*, 2019, **141**, 8584.

Aubrey R. Paris responded: It seems likely that intermediate binding energies are at least partially responsible for the results that we see using these intermetallic *versus* distinct metal species. In fact, we are currently finishing up a project which we believe provides experimental evidence for multi-metal catalyst surfaces altering binding energies (*i.e.* compared to the individual constituent metals) for frequently invoked intermediates. So stay tuned for that!

Andrew B. Bocarsly remarked: The two approaches presented in these two papers provide excellent examples of a long debated solar fuels conversion dichotomy. Namely, does the best engineering of a solar fuels system utilize a "single pot" photoelectrochemical cell or is a better system obtained by interfacing a photovoltaic panel to an electrochemical cell containing an optimized electrocatalyst? Please discuss the pros and cons of these two approaches for CO_2 reduction and indicate which approach is preferred.

Aubrey R. Paris replied: Choosing whether an electrochemical or photochemical approach is "preferred" depends largely on one's goal for the research. If the goal is to create a system that could be industrially implemented immediately, electrochemical CO_2 reduction has an upperhand, because much more progress has been made in electrochemical catalytic systems in recent decades. Indeed, many desirable products are already achievable at impressive Faradaic efficiencies using electrocatalysts. This certainly doesn't mean that photoelectrochemical CO_2 reduction research should be abandoned, but it simply doesn't boast the same amount of progress as the electrochemical analog. That said, with more fundamental research, photoelectrochemistry has the potential to help address one of the lasting challenges of electrochemical CO_2 reduction: impractical overpotential requirements.

Wilson A. Smith replied: In the short term (which is the time frame where solutions are needed), the best approach has to be renewable electrolysis (where an electrolyser can be powered by any renewable electricity supply – not just PV) over direct photoelectrochemistry. The technological development of PV panels is too robust, and large electrolysers already exist, but are expensive. However, large CO_2 electrolysers do not exist, so significant efforts should be made towards developing these by translating fundamental lab scale research to an industrial scale. On the other hand, the PEC approach still not only suffers from low efficiencies and material stability issues, but even in the best case scenarios no real upscaling has been done at a practical level. While this avenue should still be interesting to pursue, it may only be viable in a long term timeframe (at best). Therefore the fastest way to engineer a solar fuel system is to use two known and scaled technologies instead of one unproven technology that has never been made at a large scale.

Sergii I. Shylin opened a discussion of the paper by Chia-Yu Lin: Do you get chlorine as a by-product at the anode when electrolyzing seawater?

Chia-Yu Lin replied: We did not notice chlorine generation in this work.

Moritz F. Kuehnel enquired: What is the mechanism by which the electrode corrodes? Is it formation of hypochlorite?

Chia-Yu Lin responded: In the case of the unmodified $CaFeO_x$ electrode, both formation of hypochlorite and low bulk solution pH (<6) after long-term electrolysis are the main reasons for the destabilization of $CaFeO_x$. On the other hand, low bulk solution after long-term electrolysis destabilized $FePO_4$-modified $CaFeO_x$.

Andrew B. Bocarsly asked: You noted that the ocean is buffered around pH 8. This is due to the presence of a borate buffer system. In your synthetic sea water, it appears that borate is not present. Do you expect this to affect your experimental results, given that borate layers have been shown to impact other electrode systems?

Chia-Yu Lin replied: We used phosphate (0.5 M) buffered seawater solution for our experiments. The phosphate concentration is much higher than borate, so its effect would be small. However other ions, such as Mg^{2+}, indeed have a negative effect.

Andrew B. Bocarsly continued: A current density of 10 mA cm^{-2}, is often selected as the operational value for a photoelectrochemical cell. In this specific case, why have you selected this value? Did you rule out the use of focused sunlight?

Chia-Yu Lin replied: We would like to apply this catalyst for photoelectrochemical water splitting in the near future, so we selected a current density of 10 mA cm^{-2} as our applied current density in this work.

Erwin Reisner enquired: You have reported water oxidation to O_2 in the presence of salt water. What is your opinion about the potential economic advantages to oxidising chloride to Cl_2 or other chlorinated products instead? This would allow the solar-driven production of two valuable products – H_2 from aqueous protons and a potentially value-added product from oxidation.

Chia-Yu Lin responded: I think it will be great of interest. Nevertheless, some issues should be addressed. Making chlorine from seawater/salt water should be under acidic conditions, and in this context, a noble metal for chloride oxidization should be used.

Michael Grätzel asked: Are you trying to make a water oxidation catalyst that works best in neutral solution? If so, one compartment of the electrolyzer would be neutral and the other one basic, This is a challenge for the bipolar membrane that would have to be used to separate the two compartments of the electrolyser. As a result there would be additional overvoltage losses. Have you tested your system at pH 0? What pH are you testing? Natural seawater? Not acidified?

Chia-Yu Lin answered: Yes, we tried to develop electrocatalysts for both OER and HER at neutral pH. We did not use a electrolyzer with two compartments with different pHs. In addition, all of the experiments in this work were performed in phosphate (pH 7) buffered electrolytes.

Andrew B. Bocarsly enquired: Given that iron phosphates are reasonably soluble in water, how do you plan to stabilize this surface in seawater? Will your approach require the addition of substantial quantities of phosphate buffer to the electrolyte?

Chia-Yu Lin responded: In this case, sufficient phosphate should be added to the seawater to stabilize the iron phosphate, and of course, this is the limitation of this electrode.

Christine A. Caputo opened a discussion of the paper by Ulf-Peter Apfel: I am curious about your choice of activity comparison – the NiP system with carbon nitride and carbon quantum dots you used for benchmarking the activity of your system. Being an author on both those papers (ref. 1 and 2), I would say that they are not the highest activity systems and so make a weak argument for comparison. Do you think your low activity is just due to the low reduction potential in your system? Is there a way to tune the bandgap of your material?

1 G. A. M. Hutton, B. Reuillard, B. C. M. Martindale, C. A. Caputo, C. W. J. Lockwood, J. N. Butt and E. Reisner, *J. Am. Chem. Soc.*, 2016, **138**, 16722.
2 C. A. Caputo, M. A. Gross, V. M. Lau, C. Cavazza, B. V. Lotsch and E. Reisner, *Angew. Chem. Int. Ed.*, 2014, **53**, 11538.

Ulf-Peter Apfel responded: I personally believe that the low activity is due to the low reduction potential in our system. A possible pathway to further tune the bandgap would be, *e.g.* variation of the metals as well as of the chalcogenides. We are currently investigating such possibilities and hope to find out soon if this is possible.

Christine A. Caputo asked: I have a question about the stability of your systems. Carbon nitride and carbon quantum dots are very stable photosensitisers, in fact we found with those materials that this is quite a challenging experiment to design. It is difficult to find a molecular catalyst that lasts as long as some of the latest photosensitizer materials and will allow for long-term stability studies in hybrid systems. Have you tested your system for long-term stability?

Ulf-Peter Apfel replied: This is a good and very important point. We solely tested the long-term stability under electrochemical conditions. Here, we do not have a problem with long-term stability and the materials operate for more than 3 weeks without decomposition or loss in activity. For the photochemical experiments with the molecular catalysts, we never tested the stability since the shown activity is just too low.

Daniel Antón-García commented: Looking at the Mott–Schottky analysis, there is not enough driving force for H_2 production. You also use NiP, which requires an additional 200 mV of overpotential to produce H_2. Where is this driving force coming from? And why is it that NiP outperforms Pt, which is known to: a) be a more active catalyst and b) require less driving force?

Ulf-Peter Apfel answered: As we discuss in our manuscript, the conduction band minima of all our samples are very close to the hydrogen potential, thus a low hydrogen evolution activity is expected. Interestingly, we found that with NiP decoration hydrogen evolution was observed, however not with Pt decoration. We do not know yet why those two modification behave so differently on our materials, which is one focus of our ongoing work!

David Wakerley said: You present an interesting way to mimic enzyme active sites on a heterogeneous surface. The enzyme active site is quite flexible – will the loss of flexibility on the heterogeneous catalyst present any issues?

Ulf-Peter Apfel responded: The heterogeneous surfaces are still quite flexible. The presented Fe/Ni sulfides for example show an opening of coordination sites at the Fe/Ni centers, concomitant with sulfide loss, at reductive conditions. The catalytic species here is only provided at catalytic conditions – in my mind this is very good compared with an enzyme active site. However, you are absolutely right, the degree of flexibility is reduced compared to that of an enzyme. I personally believe that this is not an issue.

Sylvestre Bonnet asked: Do you have any idea about the type of contact between the solid photosensitising material and the catalyst in solution? Is there any form of adsorption, or is photocatalysis running *via* a form of dynamic quenching?

Ulf-Peter Apfel replied: No not yet. This is something we are currently investigating.

Vivek Badiani commented: What is your opinion on a top-down *vs.* bottom-up approach to material synthesis? What is the flexibility available for the tuning of the materials akin to ligand tuning?

Ulf-Peter Apfel replied: I do not think that there is a big difference between top-down *vs.* bottom-up approaches for material synthesis. Both have specific advantages and disadvantages and none of us currently know the right pathway to gain highly active and robust catalytic materials. I believe that scientists should follow their own ideas without thinking about such things. Concerning the flexibility of the ligand tuning, one always has to ask himself for what purpose this is done. If you aim for an application but you establish a twenty-step synthesis, I hardly can believe that this will go into an industrial application. If you do such things for gaining knowledge on how things can be done, tuning ligands is a wonderful method to understand the underlying principles. There is always a fine line between basic and application driven research. This has to be balanced and communicated openly without any hesitation.

Vivek Badiani commented: You present an interesting take on bioinspiration, are there any other natural active centres you may look to to mimic as catalysts?

Ulf-Peter Apfel replied: Thank you for you comment. We are currently mainly looking for reductive systems such as hydrogenases, CO dehydrogenase and nitrogenases. But I am sure that there will be plenty of interesting systems in the future that we and others have not thought about yet. As an additional example for such a strategy, I want to highlight the work of Philipp Kurz who is using a comparable strategy to ours to mimic the OEC cluster. I am certain that many more catalytic processes can be found where a bioinspired approach might lead to a rationally designed and applicable catalytic system.

Andrew B. Bocarsly enquired: Iron sulfides are characterized as having highly defective crystal structures. This is typically due to the mobility of the metal ions in these structures. Does this play a role in your material's conductivity or doping levels?

Ulf-Peter Apfel responded: This is likewise the case here, but the crystallographic structure of pentlandite is not comparable, *e.g.* with those of FeS2 or NiS. Operando spectroscopy, as well as scanning electrochemical cell microscopy, data indicate that it is the mobility of sulfur/ creating sulfur "holes" instead of the metal mobility that plays a significant role in such materials for their activity. The conductivity, however, seems to be unaffected by such defects.

Andrew B. Bocarsly continued: Given that you have obtained Mott–Schottky plots for your electrodes, you have the data needed to calculate the carrier concentration. Is that value available?

Ulf-Peter Apfel responded: The value is currently not available. But this is a very good point and we will have to determine the carrier concentration now to further receive information on our system.

Michael Grätzel asked: Could your please provide a mechanism that would explain the lower Tafel slopes for H_2 evolution on your Ni/Fe sulfide catalyst compared to that for Pt (30 mV/decade for the Vollmer–Tafel mechanism)?

Ulf-Peter Apfel answered: The Tafel slopes for the Ni/Fe sulfide are not smaller than that for Pt. In addition, the mechanism for the H_2 formation of such sulfides is very different from that of Pt as we could show by operando NRIX measurements. It rather looks like a mechanism that resembles that of [FeNi] hydrogenases rather than that of Pt.

Joost N. H. Reek added: I would like to ask a more philosophical question. In the introduction you use the active site of enzymes such as hydrogenase as inspiration for the preparation of your heterogeneous catalyst materials. The question is whether this is the correct source of inspiration, as the active site only is not a good catalyst. There are thousands of hydrogenase mimics but all require a relatively large overpotential for proton reduction catalysis. Work by Lubitz and Fontecave (ref. 1) demonstrated that an artificial hydrogenase mimic can be put into an apohydrogenase enzyme, restoring full activity. This shows that the activity of the enzyme is for a large part determined by the peptide environment around the active site rather then the active site. If we use just the active site as an inspiration, we may have the wrong starting point, as we do not take into account the environment.

1 G. Berggren, A. Adamska, C. Lambertz, T. R. Simmons, J. Esselborn, M. Atta, S. Gambarelli, J. -M. Mouesca, E. Reijerse, W. Lubitz, T. Happe, V. Artero and M. Fontecave, *Nature*, 2013, **499**, 66.

Ulf-Peter Apfel replied: This is a very interesting question and you are absolutely right that mimics usually operate under different conditions. The example you mentioned is a perfect one. However, if you carefully check the [FeFe]-hydrogenase mimics in solution and when incorporated into HydA, it is obvious that they reveal different structures. The structural change is, as highlighted by you, adjusted by the peptide environment. As such, a different reactivity is expected.

I do, however, believe that bioinspired mimics are still very valuable and that nature gives a lead to come up with new materials. Let me explain this further. Our material contains a cuboidal metal-sulfur structure which can be assumed as a mimic for the [4Fe–4*S*] clusters that enable electron transport in nature. Likewise to nature, our materials show high conductivity when used in electrochemical experiments. Furthermore, pentlandites reveal short metal–metal interactions that also cover the surface of the material. These structural fragments are comparable to the ones observed in nature and we could recently show that these are important for the material's reactivity. While I agree that this attempt might lead to a wrong starting point, it is one potential inspiration to build new materials and should not be excluded. In the end, we cannot forecast the reactivity of materials and require some kind of inspiration.

Leif Hammarström asked: What about the surface chemistry? Do your band energies shift with pH? Could you get more proton reduction at lower pH values?

Ulf-Peter Apfel answered: We have not tested the behavior under various pH conditions yet. This is certainly a good idea that we will investigate in the near future.

Víctor A. de la Peña O'Shea asked: In Fig. 4 of your paper (DOI: 10.1039/c8fd00173a), you compare the H_2 evolution of $Ni_3Fe_6S_8$ and $NiFe_2O_4$ using different co-catalysts (NiP and Pt). In the case of Pt you used 8 wt%. Do you know the particle size or dispersion of your Pt particles over the semiconductors? Did you consider that this high amount of Pt can lead to a shadow effect that is affecting the interaction of light with the semiconductor? Did you use other amounts of Pt?

Ulf-Peter Apfel replied: No, we have not yet investigated the particle size or dispersion of the Pt particles. The shadow effect is a very interesting hint. We did not think about this and will test this hypothesis by applying different amounts of Pt in the future.

Víctor A. de la Peña O'Shea continued: Did you observe any corrosion of your material? Did you observe changes in iron or nickel oxidation or on their proportion before and after the reactions?

Ulf-Peter Apfel responded: Yes, we did observe corrosion. By operando NRIX measurements we observed that at specific sulfur positions there is sulfur depletion. Subsequently, between two metals there is a void space that we assume is responsible for the high reactivity and can be occupied by protons just as is observed in [FeNi] hydrogenases. Until now, we have no data on the exact oxidation state during the catalysis of Fe or Ni. The proportion of both metals, however, did not change as we could show by SEM-EDX and XPS data.

Andrew B. Bocarsly commented: You indicated that your electrode has some degree of activity as a photocathode for CO_2 reduction, but little activity for H_2 formation. Is there a strategy in this materials class for developing systems that are electrocatalytic for CO_2 reduction?

You saw some CO_2 reduction, usually when looking for a good CO_2 photoelectrode one looks for a lousy hydrogen photoelectrode. Do you have any reasoning for this?

Ulf-Peter Apfel replied: Indeed, we do have a strategy to further alter such materials and to favor the electrocatalytic CO_2 reduction by these materials, *e.g.* by changing the metals and the chalcogenides. However, besides the catalyst itself, the reaction conditions are also of utmost importance and I do believe that you need the proper reactor setup (in addition to the catalyst) to facilitate and to improve a specific reaction. I believe that looking for a lousy hydrogen photoelectrode when you would like to have a good CO_2 photoelectrode is not necessarily required. Again, I personally do believe that it is likewise the reaction conditions and the material processing that can be altered to introduce different reactivities. Why not test a good hydrogen electrode under completely different reaction conditions in a different reactor?

Marta C. Hatzell said: With regard to environmental systems, minerals, sands, *etc.*, have these reactions been demonstrated in fields such as photogeochemistry?

Ulf-Peter Apfel responded: Of course. See, for example, deep sea ocean vents. Materials, *e.g.* stable alloys, can be found here that catalyze various reduction processes. Under normal conditions such alloys would normally be surface oxidized and not very reactive. As such, I believe that the environmental conditions indeed aid changing redox properties and also stabilize the reactive intermediates (or at least do not trigger their decomposition).

Michael Grätzel commented: A few years ago there was lots of excitement in the scientific community about the virtues of MoS_2 as a hydrogen evolution catalyst. How does your Fe/Ni sulfide compare with MoS_2?

Ulf-Peter Apfel replied: While comparing two distinct different sulfides is certainly desired, such a comparison is very difficult, probably misleading and simplifies the problem set too much. The structure of Fe/Ni pentlandite is not at all comparable with MoS_2 and results in different properties of this material. In contrast to MoS_2, the bulk pentlandite is highly conductive due to its unique structure. In addition, pentlandites are very stable under acidic and basic conditions as long as they are kept under reductive conditions. Likewise, the mechanisms of both materials in generating hydrogen seem to be very different. I believe, however, that the major difference (and probably an advantage for application) between pentlandites and MoS_2 is that with the Fe/Ni sulfides we do not require a specific nanostructure to achieve good activity.

Katarzyna Sokol asked: Have you tried or considered other synthesis methods for the particles in order to make them smaller and better control their size? With such a degree of aggregation, and particle sizes in the range of hundreds of nanometers, you will be losing the quantum size effects, and the band gap and conduction band edge should be close to the bulk material. Is there an advantage of using the particles in this case, with so many alternative electrode film deposition methods available? Have you considered making the particles smaller, in the range of 10 nanometers or less, to increase the band gap and possibly shift the conduction band edge to be more negative?

Ulf-Peter Apfel answered: We attempted the synthesis by various methods. The major problem is, however, that the pentlandite has a high temperature phase and low temperatures usually facilitate the formation of other phases. So the formation of defined nanoparticles is a borderline problem. Unfortunately, there are currently no electrode film deposition methods available for this particular material. We are currently working on this issue to make thin films. But at the moment, we have not achieved this goal.

Anna Hankin said: Could you comment on the accuracy of using the Mott–Schottky approach for determining the band edge positions in your materials, especially since the charge carrier densities in the materials are not known? Have you tried to compare Mott–Schottky results with other measurements, such as chopped photocurrent?

Ulf-Peter Apfel answered: My personal impression is that the Mott–Schottky approach is very cumbersome and error-prone. Small variations during the impedance measurements can lead to significant alterations. As such, I do expect a non-negligible error of the presented values. We have not yet measure chopped photocurrents but will certainly perform this measurement.

Andrew B. Bocarsly remarked: From an experimental point of view, the flat band potential is best determined using light intensity dependent open circuit photopotential measurements. This technique avoids the unknown impedances, and frequency dependence of the Mott–Schottky analysis.

Ulf-Peter Apfel responded: You are absolutely right and we plan to do this in the near future.

Flavia Cassiola commented: The material you reported has intriguing properties that should be investigated further as proposed in your paper. During the discussion you commented that the stability of $Fe_3Ni_6S_8$ is not high on your priority list at the moment because the material is considered very cheap and its replacement is consequently not an issue. Thinking ahead, as you develop the potential of the $Fe_3Ni_6S_8$ photocatalytic activity (with or without co-catalysts), one suggestion would be to consider stability and durability of the material in the earliest stages of development. Although the material is cheap and abundant, in a real device in an industrial scale the material should not be replaced in every reaction cycle. One suggestion is to consider stability studies as you proceed with future developments (band gap tuning of the pentlandites, nanoengineering of the particle sizes and further optimization of their elemental compositions as improvements on photocatalytic properties). How would you speculate on the stability of the material with your results and at your current development stage? Does this insight on stability change your current ways of thinking regarding the application of $Fe_3Ni_6S_8$ in a photosynthesis device?

Ulf-Peter Apfel replied: You are absolutely right pointing out that stability is one of the most important parameters for an industrial application. We solely investigated the stability under electrochemical conditions. Herein, stability is not an issue. After talking to some of my industrial partners I am currently not convinced, however, that photocatalytic applications for hydrogen generation will enter industry soon. As such, I did not focus too much on the stability of this material but was rather curious as to whether we can trigger a photocatalytic process with it. It is definitely on my to-do list to also investigate the stability in the near future with a better material and I am certain that, likewise to electrocatalysis, stability is not an issue. But still, even a high stability of our material under photocatalytic conditions would (at the moment) not change my mind regarding its application in a photosynthetic device.

Peter Brueggeller said: At this conference the question of what the best way to find potential photocatalysts is has arisen. One rationale is that the electrocatalytic activity is often only a calculated number, *e.g.* a theoretical proton reduction with a turnover frequency of more than 100 000 per second has been calculated for some DuBois' catalysts in ref. 1. However, the corresponding photocatalytic activity in the form of experimental hydrogen production analysis only leads to a TON of 11.4. Since the compounds in U.-P. Apfel's paper (DOI: 10.1039/c8fd00173a) show an interesting electrocatalytic behaviour with a possible photocatalytic application, I wonder whether the authors of this session could comment on the differences between theoretical electrocatalytic activities and resulting experimental photocatalytic hydrogen determinations.

1 M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois and D.L. DuBois, *Science*, 2011, **333**, 863.

Ulf-Peter Apfel responded: I am not certain if one should really compare photocatalytic and electrocatalytic conditions. The reaction conditions applied are very different. While an electrocatalyst should be potentially capable of performing this reaction also under photochemical conditions, this is not always the case and usually the photosensitizer and sacrificial electron donor are an important component that do not always receive the right attention when discussing different TON/TOF values. In addition, likewise the product composition can be altered as was shown by the Robert group with their photo- *vs.* electrochemical CO_2 reduction experiments (ref. 1–3).

1 H. Rao, L. Schmidt, J. Bonin and M. Robert, *Nature*, 2017, **548**, 74.
2 H. Rao, C. -H. Lim, J. Bonin, M. Miyake and M. Robert, *J. Am. Chem. Soc.*, 2018, **140**, 17830.
3 H. Takeda, H. Kamiyama, K. Okamoto, M. Irimajiri, T. Mizutani, K. Koike, A. Sekine and O. Ishitani, *J. Am. Chem. Soc.*, 2018, **140**, 17241.

Andrew B. Bocarsly posed a question to Ulf-Peter Apfel and Chia-Yu Lin: Both of you use earth abundant elements in your semiconducting electrodes, but show that these materials introduce all kinds of new complications with respect to electrode stability and response. Do you believe that we are better off using more expensive materials which exhibit fewer electrochemical complications or should our studies continue with less expensive materials and engineer them to be "good" materials?

Ulf-Peter Apfel replied: I personally believe that it is a necessity to proceed with earth-abundant metals/materials. While we certainly do have issues with the stability now, I am convinced that we can overcome these problems. We need materials that are abundant to reduce the current investment costs and to push electro- and photo-chemical devices out of a niche existence into large-scale technology.

Chia-Yu Lin answered: Noble metals do indeed have better performance in most cases, but in some cases, noble metals cannot solve our problems, such as mitigation of chloride oxidation. In addition, some reactions require less expensive materials to activate. Therefore, both kinds of material require further investigation.

Conflicts of interest

There are no conflicts to declare.