

Inorganic assembly catalysts for artificial photosynthesis: general discussion

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Hiromu Kumagai opened a discussion of the paper by Akihiko Kudo: Do you have any strategy to suppress CO evolution from RGO which was used in the Z-scheme system, such as substitution of some compounds? In water splitting using similar Z-scheme configuration with RGO, does same oxidation of RGO to form CO progress?

Akihiko Kudo answered: In the present system, we used TiO₂ that has strong oxidation power due to the deep valence band. That is the reason why a part of CO forms by oxidation of RGO. If you employ an O₂-evolving photocatalyst with a shallower valence band such as BiVO₄, the undesirable oxidation is suppressed.

Hiromu Kumagai asked: Why do similar Z-scheme systems show different behavior for RGO oxidation between using in water splitting and in CO₂ reduction?

Akihiko Kudo answered: In the previous literature for water splitting,¹ H₂ and O₂ simultaneously evolved in a stoichiometric amount. In that case, the Pt cocatalyst was loaded on CuGaS₂. In contrast, when the Pt cocatalyst is not loaded in the present CO₂ reduction, the ratio significantly deviated from 2 : 1 for water splitting under Ar, and RGO oxidation also proceeded. These results suggest that the Pt cocatalyst works not only for H₂ evolution on CuGaS₂, and probably for hole transfer from CuGaS₂ to RGO, but also suppression of the RGO oxidation in water splitting.

1 K. Iwashina, A. Iwase, Y. H. Ng, R. Amal and A. Kudo, *J. Am. Chem. Soc.*, 2015, **137**, 604.

Katsuhiko Takagi said: When we construct the Z type-scheme system for CO₂ reduction by semiconductor catalysis, many factors are considered to increase the efficiency of the photocatalyst reduction. In particular, as one of the most crucial factors, the electron transfer rates for both half cells should be balanced so as to possess equal rates, otherwise the generated redox intermediates should disappear by a back-electron transfer. What do you think of the requirement of this matching of the electron transfer rate?

Akihiko Kudo answered: Yes, your comment is correct. The matching of electron transfer in a photoelectrochemical cell is recognized well. It can be controlled to adjust the balance by optimizing the size of the photoelectrodes taking the efficiency into consideration. The mismatch may be the reason why the efficiency of a photocatalyst system is low. We might control it by optimizing the amounts of reduction and oxidation photocatalysts, and the contact between the photocatalysts.

Haruo Inoue remarked: We recognize that you found for the first time photochemical CO₂ reduction on a semiconductor with silver on it. This time you also found that metal sulphide can reduce CO₂. Considering the “Kudo-library of photocatalysts” which you have been constructing, could you provide your opinion regarding what are the factors controlling CO₂ reduction?

Akihiko Kudo answered: Catalytic properties of the surface of photocatalysts and cocatalysts are key issues. Electrocatalysts for CO₂ reduction are informative. Actually, an Ag cocatalyst we have reported¹ is also an effective electrocatalyst for CO₂ reduction to CO. It implies that an electrocatalyst can be used for a cocatalyst.

1 K. Iizuka, T. Wato, Y. Miseki, K. Saito and A. Kudo, *J. Am. Chem. Soc.*, 2011, **133**, 20863.

Dong Ryeol Whang asked: Is there any possibility that RGO is acting as a catalytic active site for CO₂ reduction in your system? RGO or GO themselves have been known to reduce CO₂. It was mentioned that the CO produced from a RGO–TiO₂ sample (entry 4, Table 2 in the paper) was due to the side reaction from RGO, however, can you provide some evidence, *i.e.*, isotope labeling?

Akihiko Kudo replied: Our control experiments have concluded that RGO did not work as a catalytic site for CO₂ reduction and also for water reduction. The CO formation shown in entry 4, Table 2 is due to RGO oxidation. We observed 12CO using 13CO for entry 1, though we did not check it for entry 4. But, the possibility of CO₂ reduction on RGO is low, because the similar amount of CO was obtained in entry 5 under Ar.

Etsuko Fujita asked: Obviously RGO absorbs visible light when you carry out photocatalytic CO₂ reduction using your RGO–TiO₂ composite. How much are photons absorbed by RGO?

Akihiko Kudo replied: Yes, it absorbs incident light. It is confirmed from the absorption spectrum that the shielding effect toward incident light is not significant using the optimized amount of RGO.

Etsuko Fujita commented: Can you replace the RGO of your RGO-TiO₂ composite with transparent and conductive materials such as ITO?

Akihiko Kudo answered: Yes, we can use it. We have preliminary positive results using other conductive materials.

Alexander Kibler asked: Do you attempt to control the particle size, morphology or crystallinity of the metal sulphides or the RGO-TiO₂ composite powders that you are preparing? It is well reported that modulation of these parameters can enhance catalytic performance or even change catalytic pathways.¹ Do you expect any changes in the catalytic activity if you were to change any of these factors?

1 (a) I. Lee, F. Delbecq, R. Morales, M. A. Albitar and F. Zaera, *Nat. Mater.*, 2009, **8**, 132–138; (b) U. Hartfelder, C. Kartusch, M. Makosch, M. Rovezzi, J. Sá and J. A. van Bokhoven, *Catal. Sci. Technol.*, 2013, **3**, 454–461; (c) D.-G. Tong, W. Chu, Y.-Y. Luo, X.-Y. Ji and Y. He, *J. Mol. Catal. A: Chem.*, 2007, **265**, 195–204.

Akihiko Kudo replied: The particle size, morphology and crystallinity of heterogeneous photocatalysts are important factors affecting photocatalytic performance. The particle size and morphology will be significant, especially in the present system in which contact or collision between CO₂-reducing and O₂-evolving photocatalysts is indispensable for inter-particle electron transfer. The significance of crystallinity depends on a photocatalytic reaction. Unfortunately, we do not systematically examine those factors yet.

1 A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253.

Hisanao Usami said: You presented the concept to integrate two photocatalysts with conductive RGO to produce the Z-scheme model, such as the TiO₂-RGO-CuGaS₂ triad system. RGO is a conductive material which can mediate electron transfer from the conduction band of the photo-excited TiO₂ to the valence band of the photo-excited CuGaS₂. However, the RGO can also mediate back-electron transfer from the conduction band to the hole in the valence band of the TiO₂. Why can the RGO promote the forward electron transfer? Could you comment on what is the key factor to control the direction of electron transfer in the RGO?

Akihiko Kudo replied: RGO enhances not only forward electron transfer but also backward electron transfer. When a suitable p-type photocathode is connected with an n-type photoanode using an electric wire in a photoelectrochemical cell, the system works for water splitting under no bias condition. Our system consists of p-type CuGaS₂, n-type TiO₂, and RGO. In this system, RGO works as an electric wire as in a photoelectrochemical cell. So, our system works as a micro-electrochemical cell. So, the key issue to promote the forward electron transfer is to employ p and n-type materials as photocatalysts.

Dogukan Hazar Apaydin opened a discussion of the paper by Young Soo Kang: As it was indicated in the paper of Bocarsly *et al.*¹ from 2010, the mechanism goes over multiple steps where the pyridinium ion acts as an electron shuttle. This

concept was proved by several other papers. In the light of these could you comment on the reasoning behind immobilizing the catalytic moiety in a polymer?

1 E. B. Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev and A. B. Bocarsly, *J. Am. Chem. Soc.*, 2010, **132**, 11539–11551.

Young Soo Kang responded: In PVP, the N-heterocyclic moiety can make a complex with CO₂, increasing the energy of CO₂ and lowering the activation energy for the first electron transfer reaction, which is the rate determining step of CO₂ reduction reaction.

Dogukan Hazar Apaydin asked: I agree with the fact that the pyridinium is the electron shuttle. Hence my question is; if the desired product is methanol and the requirement for this product is 6 electrons, why would you like to immobilize it? I guess when immobilized the process will stop at the stage of formic acid or formaldehyde.

Young Soo Kang answered: When CO₂ is immobilized with PVP by complexation with the N-heterocyclic moiety of PVP, the activation energy for the first electron transfer reaction of CO₂ reduction reaction. This is the rate determining step of the CO₂ reduction reaction. The next 5 step reduction processes can occur by a concerted mechanism due to the lower activation energy of electron transfer. The problem is the proton transfer reaction to make methanol because this reaction needs six electrons and six protons to produce methanol. This is why we used a Nafion layer as the outermost layer of the electrode surface.

Jose Martinez remarked: Have you considered using another surface besides Pt? There might be a mediated transition state between Pt and pyridine/pyridinium that results in catalysis. There is evidence for this in work done by Andrew B. Bocarsly. I would advise using a glassy carbon surface or a similar surface that is not inherently catalytic.

Young Soo Kang replied: We have not tried with anything other than Pt as the electrode. We will do more according to your comment later on.

Dogukan Hazar Apaydin asked: You have mentioned that the electrode of choice in your study was platinum-coated FTO glass. What is the reason behind this? Is Pt required for the catalytic activity of pyridinium?

Young Soo Kang responded: Yes, Pt can be used as an excellent candidate metal for the PVP adsorption to make a stable electrode.

Can Li commented: What is the main product you obtained? Was it methanol or formaldehyde?

Young Soo Kang answered: In this electrochemical reaction, we have formaldehyde as a major product. It is interpreted as the reduction potential of CO₂ to formaldehyde is tuned in this electrochemical reaction.

Can Li remarked: The stability of organic polymer should be considered. Did you observe the oxidation of the polymer during the photochemical process?

Young Soo Kang answered: PVP is quite stable for the photochemical and photoelectrochemical reaction. It was durable for 4–5 days with one sun light irradiation. We have not checked yet for longer than 5 days.

Akihide Iwase opened a discussion of the paper by Hyunwoong Park: Regarding the claim that the durability (stability) of CdS was improved by coupling with titanates, please kindly explain the mechanism in more detail.

Hyunwoong Park responded: CdS is notorious for photocorrosion, primarily because of sluggish charge (*i.e.*, holes) transfers. Coupling with titanate is expected to enhance the transfer of photogenerated charges in CdS. Furthermore, a significant fraction of CdS is located inside of the titanate, which effectively blocks unwanted photoreactions. A further study is needed.

Sang Ook Kang said: Since you mentioned about the confusion coming from the use of isopropanol (IPA) that can be a source of hydrogen, have you tried an alternative scavenger chemical?

Hyunwoong Park answered: We have not tested other organic hole scavengers. Our previous study revealed that 2-propanol was the best at enhancing the photocatalytic activity among five scavengers (methanol, ethanol, triethanolamine, EDTA, and 2-propanol).

Haruo Inoue asked: This is a minor point, but I have a little concern about the effect of the concentration of IPA. When you added IPA to D₂O and compared the effect of the concentration of IPA in your semiconductor hydrogen evolution experiment, you have detected H₂ in the case of 5% IPA, while HD was detected in the case of 30% IPA. You have concluded from the results that the α hydrogen atom of the C–H bond in IPA serves as the proton source. I partly agree with that, but the deuteron and proton of D₂O and IPA are already equilibrated and thus quantitative estimation of the H₂/HD ratio should be required for this conclusion. How about it?

Hyunwoong Park answered: The relative abundance of D/H (units of vol%) from the IPA/D₂O (v/v) solutions is given by $D/H = [1.11 \text{ g mL}^{-1} \times (100-x) \text{ mL} \times 2/20 \text{ g mol}^{-1}] / (0.786 \text{ g mL}^{-1} \times x \text{ mL} \times 8/60 \text{ g mol}^{-1})$. When $x = 5\%$, the D/H abundance is ~ 20 and D₂ is likely to be the only measurable hydrogenic species. In contrast, when $x = 30\%$, the D/H abundance decreases to ~ 2.5 , and D₂, DH, and H₂ can be found together with a probable intensity order of D₂ > DH > H₂. In agreement with this speculation, with 5% IPA, the headspace gas sampled after 2 h showed the evolution of D₂ ($m/z = 4$), and the signal intensity sampled after 5 h became stronger. Neither HD nor H₂ were found (Fig. 5a of our paper). Accordingly, the H₂ produced in this study (Fig. 4 of our paper) came from water, and the as-synthesized Pt/CdS/TNTs were capable of splitting water. However, when the concentration of IPA was increased to 30%, DH and D₂ were measured in the 2 h- and 5 h-samples, and there was no signal for H₂ (Fig. 5b). This suggests

that the contribution of protons released from IPA on the hydrogen production cannot be ignored at high IPA concentrations. A number of papers focus on photocatalytic H₂ production in the presence of sacrificial alcohols at high concentrations (*e.g.*, 50 vol%); the amount of H₂ reported in these studies appears to be overestimated.

Can Li remarked: Why or how is methane produced?

Hyunwoong Park answered: We have found evidence that the methyl radical is produced in aqueous CdS solution under visible light. A ¹³CO₂ experiment further confirmed the production of ¹³CH₄.

Can Li commented: Very few papers have reported methane production. What is the special difference between your system and others? Why is no methanol or formaldehyde formed before methane production?

Hyunwoong Park answered: The surface states (binding mode and intensity of CO₂, Lewis acidity, porosity, *etc.*) appear to be important. There are many papers for methane production from CO₂ in aqueous media; however, their results were not reproducible when we repeated the experiments.

Kristine Tolod opened a discussion of the paper by Fabio Di Fonzo: I understand from your paper that you used electrodes with a geometric area of 0.9 cm². Have you ever tried working with a bigger geometric area? As is the case for thin films, uniformity and continuity of the film on the surface of ITO or FTO becomes an issue, when working with bigger geometric areas, and this is a potential issue when we think about scaling up the system. What are your experiences on this?

Fabio Di Fonzo replied: We tried up to 25 cm² devices and the major issue we faced is the resistivity of the FTO glass used. No major problems with the deposition of the layers arose.

Joshua Karlsson asked: In your paper, you are consistently making a point about stability of the hybrid organic/inorganic photocathode. How would the stability be affected in a real device, which is subject to changes in temperature? Would an increased number of defects at higher temperature for example lead to a drastic decline in performance?

Fabio Di Fonzo replied: The science and technology of hybrid organic/inorganic photoelectrochemical devices, HOPEC, is still in its infancy and no data about outdoor testing, real or simulated, are available. Nevertheless, the literature of organic photovoltaics has been focusing recently on this issue. Few papers¹⁻⁴ have been dedicated to the study and standardization of outdoor testing of OPV. In general, a consensus emerges that a two years lifetime with performances within 80% of the initial values are achievable when oxygen is prevented from entering into the device with proper encapsulation. For what concerns HOPEC devices, the main issue will be assessing the effects of long term exposure of the organic semiconductors to water, even if I have to mention that so far the biggest issues in this respect arose from the inorganic layers, mainly the hole selective contact.

For what concerns the specific effect of temperature, it has been reported³ that OPV show a positive temperature coefficient even if specific damages may be caused depending on the specific architecture and materials used.⁵

1 M. Corazza *et al.*, *Sol. Energy Mater. Sol. Cells*, 2015, **143**, 467–472.

2 D. Angmo *et al.*, *Energy Technology*, 2015, **3**, 774–783.

3 N. Bristow *et al.*, *J. Renewable Sustainable Energy*, 2015, **7**, 013111.

4 C. Owens *et al.*, *Polymers*, 2016, **8**, 1.

5 M. Corazza *et al.*, *Adv. Energy Mater.*, 2016, **6**, 1501927.

Haruo Inoue commented: In your photocathode system, you have electrochemically injected electrons to the conduction band of WO_3 prior to the photoexcitation and the injected electron serves as the carrier in the photocathodic current. In Fig. 1 of your paper, you show the irreversible cathodic electron flow. Is there any possibility that the excitation of P3HT injects an electron to the conduction band of adjacent WO_3 to suffer the back electron transfer to the valence band of P3HT, which could be competing with the expected irreversible electron injection to the conduction band of another adjacent PCBM?

Fabio Di Fonzo replied: Even if from a thermodynamic point of view electron injection from the P3HT to the WO_3 is possible, this is kinetically unfavourable due to the very large misalignment between the LUMO of the P3HT and the conduction band of WO_3 , which is indeed close to the HOMO of the first favouring electron injection from the oxide to the polymer.

Dogukan Hazar Apaydin asked: We know from the OPV that in some cases annealing of the active layer helps to increase the photocurrent. Is it the case as well in your P3HT/PCBM catalytic system?

Fabio Di Fonzo replied: Yes it is, indeed we anneal our devices as a standard procedure.

Haruo Inoue returned to the discussion of the paper by Akihiko Kudo: May I ask Professor Kudo about H_2 evolution and CO_2 reduction? Is there any guiding principle in designing the system of selective H_2 evolution or selective reduction of CO_2 ? Of course I suppose that we cannot generalize yet, but are the H_2 evolution site and CO_2 reduction site the same or different to each other? Is a hydrogen radical generated on a cocatalyst serving as a common intermediate?

Akihiko Kudo responded: We usually try to use NiO and RuO_2 cocatalysts for water splitting that have been reported in a lot of literature, because a backward reaction to form water from evolved H_2 and O_2 is negligible on such oxide cocatalysts. RhCrOx reported by Domen¹ is an excellent cocatalyst. For sacrificial H_2 evolution, not water splitting, metallic Pt and Ru are suitable cocatalysts depending on the reactant solution, because we do not have to be careful for the backward reaction. For CO_2 reduction, electrocatalysts for electrochemical CO_2 reduction will give some ideas. Actually, the Ag cocatalyst we have reported is also a good electrocatalyst for CO_2 reduction to form CO. In many cases, atomic hydrogen should be necessary for CO_2 reduction to eliminate the oxygen from a CO_2 molecule. In this sense, H_2 evolution and CO_2 reduction sites should be on the same surface.

1 K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue and K. Domen, *Angew. Chem., Int. Ed.*, 2006, 45, 7806.

Haruo Inoue asked: Is there any light intensity effect on the selectivity? Supposing the size of the semiconductor to be several tens of nanometers, the excitation frequency would be in the order of a millisecond timescale under ordinary sun light irradiation. Is the time interval of electron generation in the conduction band affecting the reduction behaviour?

Akihiko Kudo responded: It is an interesting and important comment. Electrons and holes can be accumulated for multiple electron reduction and oxidation, because the particle size of a photocatalyst is normally between sub-micrometers and several micrometers. Particulate photocatalysts with a certain size are advantageous for such light harvesting. Actually, many heterogeneous photocatalysts work using a solar simulator. Although we do not examine the effect of light intensity on the selectivity of CO₂ reduction, it should affect it. The electron flux and the concentration of atomic hydrogen on the surface should affect the selectivity for multi-electron reduction of CO₂.

Sang Ook Kang said: Your Z-scheme is adjoined by the ITO and for the reduction a sulfide material is used. Did you expect any mobility difference from the two semiconductors?

Akihiko Kudo replied: Yes, there should be a difference in the mobility between the two semiconductors, not ITO but RGO/TiO₂ composite for an O₂-evolving photocatalyst. However, in the present system, interparticle electron transfer between RGO/TiO₂ and the sulfide material is the rate-determining step. So, I do not think that the mobility in each particle is not so important.

Sang Ook Kang then returned to the discussion of the paper by Young Soo Kang: What is the determining factor that can control catalytic activity, the interface or the morphology?

Young Soo Kang answered: In this system, the thickness of PVP is one of the critical parameters to control the efficiency of the CO₂ reduction reaction. And also the even coating and interface defect can be another parameter to decrease the efficiency.

Sang Ook Kang said: Everyone wants to have a Z-scheme in hand, but in reality it is not so easy to have two photocatalytic systems simultaneously working and without doubt not to mention the efficient charge connector in-between. Along the line, what do you think is the most urgent thing to develop in terms of the items mentioned above.

Young Soo Kang answered: I think the most urgent parameter optimization is to tune the band energy of the two different photocatalytic materials to match with the electron donor and acceptor to get a highly efficient bridge to have a Z-scheme.

Fengtao Fan returned to the discussion of the paper by Fabio Di Fonzo: I have a general question on the charge separation in a hybrid material. The exciton in the organic material needs extra energy to separate from each other. What happens when you inject a electron from an inorganic semiconductor to an organic material? Will these injected carriers affect the separation of the exciton in an organic semiconductor?

Fabio Di Fonzo replied: In general, exciton dissociation consumes energy reducing the open circuit voltage of OPV and hybrid materials. Nevertheless, this is not an absolute and general truth since recently it has been demonstrated that it is possible to have OPV devices with very low voltage losses when properly selecting the materials.¹

1 D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. M. Emmott, J. Nelson, C. J. Brabec, A. Amasian, A. Salleo, T. Kirchartz, J. R. Durrant and I. McCulloch, *Nat. Mater.*, 2017, **16**, 363–369.

Christopher Windle opened a general discussion of the papers by Akihiko Kudo, Young Soo Kang, Hyunwoong Park and Fabio Di Fonzo: During the previous presentations on molecular systems, we identified that a major problem is stability. If you had to choose just one, what is the main limitation of heterogeneous catalysts right now?

Akihiko Kudo answered: Stability is not a major problem for a heterogeneous photocatalyst, especially for oxide materials. Enhancement of charge separation in a solid and suppression of charge recombination are key issues. Construction and/or introduction of efficient reaction sites will solve those problems.

Young Soo Kang responded: Yes, in both homogeneous and heterogeneous systems, durability is one of the critical problems we have to solve. In this system we used PVP and Nafion as CO₂ activator and proton transporting materials. Both of these polymers can enhance the durability of the system and we tested it for several days and proved that it is very stable. If we want to do practical work for longer than several months, we have to do more tests later on.

Hyunwoong Park answered: It depends on the aim of the heterogeneous photocatalysis (*e.g.*, energy *vs.* environmental). In the energy application (*e.g.*, solar hydrogen and CO₂ conversion), the efficiency should be the most urgent issue to be addressed. In the environmental remediation, the efficiency is less critical than the durability or applicability. For example, TiO₂, a white pigment, exhibits an excellent performance in water and air cleanup processes under natural sunlight. Nevertheless, it has not been commercially applicable yet because the recovery of slurry is still expensive. Conversely, in the solar fuel field, the efficiency matters and the entrance level to market is ~10%.

Kazunari Domen remarked: Stability is an important factor similarly to the solar-to-hydrogen energy conversion efficiency and scalability. The photocatalyst sheet based on La- and Rh-codoped SrTiO₃ and Mo-doped BiVO₄ is operationally stable, at least for several days under continuous irradiation. Some photocatalytic

systems evolve hydrogen and oxygen continuously over several months. Nevertheless, degradation and stabilisation of photocatalytic systems should be examined carefully depending on materials and reaction conditions. In practice, used particulate photocatalyst sheets are to be exchanged with new ones periodically because they can be handled easily unlike powder suspensions. A lifetime of one year is a reasonable target for particulate photocatalyst sheets.

Akihiko Kudo commented: Recycling is also an important issue. Powder material-based systems will be advantageous for the issue.

Osamu Ishitani said: I agree with Professor Kudo's comment. Research studies of these types of photoelectrochemical cell have just started. They contain many processes, most of which are still unknown. A typical example should be the interfacial electron transfer process. We need not only more examples but also basic research studies, especially time-resolved data.

Kristine Tolod said: Inorganic assembly catalysts also suffer from stability issues. I am working on BiVO₄-based photocatalysts for photoelectrochemical water splitting and I am specifically referring to these systems. We recently published a review about the top-performing BiVO₄-based photoanodes and tandem PEC/PV cells using BiVO₄-based photoanodes.¹ What we have seen from the literature is that the most stable BiVO₄-based photoanodes to date lasted for 7 days with a decay of 8.7% in photocurrent density. The typical stability benchmark is a lifetime of 10 years, so, if we are talking of 7 days *versus* 10 years, we still have a long way to go.

1 K. R. Tolod, S. Hernández and N. Russo, *Catalysts* 2017, 7, 13.

Akihiko Kudo commented: So, we should continue the study and we have to make a breakthrough. The stability depends not only on the materials but also the electrolytes and cocatalysts.

Tohru Setoyama responded: There are many reasons for degradation of catalytic performance. They depend on the catalyst. In our project, we are trying to understand the degree of decay coming from some reason. However there is a long road to propose some very stable catalyst; we need two or three year's life of catalyst considering its cost.

Haruo Inoue commented: The rate constants of all the processes on photocatalyst semiconductors such as H₂ evolution, CO₂ reduction, O₂ evolution *etc.* except photoexcitation should be far below the diffusion controlled rate constant, that is, those processes have rather large activation energies and would be very much enhanced at higher temperature. Examining the temperature effect would thus be very crucial. It should also be meaningful to check unexpected side reactions at higher temperatures.

Fengtao Fan remarked: My question is related to the improved charge separation with increased temperature. Typically, the recombination of the charge separation in a bulk semiconductor will be increased when increasing the

temperature. However, charge separation in PEC system is a rather complex process and may be highly related to the surface catalytic reaction. The improved temperature will accelerate the surface reaction and hence partially affects the charge separation. The process may be reflected by the improved OCP in the system.

Hyunwoong Park responded: In photocatalysis and photoelectrochemistry, the solid/solution interfacial charge transfer is a critical step affecting the overall photoconversion efficiency. As the reaction temperature increases, this interfacial charge transfer is expected to be facilitated while reducing the activation energy barrier for the charge transfer.

Can Li asked a general question to all delegates: Please comment on the advantages of heterogeneous and homogeneous photocatalysis, and hybrids?

Elizabeth Gibson replied: With homogeneous photocatalysis, mass transport is less problematic. However, most molecular or colloidal systems reported so far require sacrificial oxidants or reductants so they are neither sustainable nor stable. A heterogeneous system is potentially more robust as multiple charges can be more readily stored, transported and delivered to the catalyst and there is potential for either a wired or wireless system. However, diffusion can be a problem. A hybrid system has the potential advantages of both the selectivity of a molecular catalyst coupled with stability and the means to store the charge of a semiconductor. These systems are typically modular, providing the opportunity to optimise each component (absorber, scaffold and catalyst). A photoelectrochemical system, where the anode and cathode are separated, has the advantage of separating the products (*e.g.* H₂ and O₂). In each case the kinetics need to be carefully balanced. Ultimately, the winner will be the system which best handles the generation of single electron-hole pairs (*i.e.* light absorption) combined with complex redox chemistry (*i.e.* catalysis).

Rengui Li answered: For heterogeneous photocatalysis, although the efficiency is still at a very low level at the moment, the utilization of earth-abundant semiconductors and long-term stability have been attracting much attention, as it is recognized as an equipment-simple and low-cost solution for practical scalable solar hydrogen production in the future. It remains challenging to achieve efficient overall water splitting on semiconductor-based photocatalyst with the absorption range larger than 600 nm. For homogeneous photocatalysis, many effective molecular-based photocatalysts possess very high TOF and TON, some of them give even higher TON than in nature. It is essentially important for investigating the intrinsic mechanism of photocatalytic processes using a homogeneous system as the structure of a molecular-based photocatalyst are clearer than heterogeneous system. In addition, many molecular-based photocatalysts could be used as efficient reduction or oxidation cocatalysts in a heterogeneous photocatalyst system. The stability and photo-degradation of homogeneous photocatalyst systems are strongly required to be improved for potential applications. Some hybrid systems build a bridge between heterogeneous and homogeneous photocatalysis, and combine the advantages of them together, which will play more and more important roles in the research of photocatalysis.

Dong Ryeol Whang remarked: Concerning the durability of heterogeneous artificial photosynthesis systems, the stability of the material itself is most important. Natural photosynthesis, however, utilizes additional strategies to enhance the durability and prolong the process: i) charge regulation to protect the photoactive sites from damage under continuous fluctuating light intensity and ii) self healing to replace damaged proteins with fresh ones. Are these strategies also applicable to the heterogeneous systems for artificial photosynthesis?

Young Soo Kang responded: Yes, durability is a very critical problem for the AP devices because they should last for longer than several months. In this work, I masked PVP and Nafion as the outer most layers for the activation of CO₂ and proton transporting materials. Both of these polymer layers can enhance the durability of the AP devices. We also tested it for several days and proved that it is very stable. But, we have not tested it for longer than a week. It should be tested later on if we have to fabricate it for the practical devices.

Akihiko Kudo commented: The strategies will be very interesting. The strategies will improve not only the durability but also the activity. The strategy i) can possibly be applied to heterogeneous systems by a suitable design of the photocatalysts. But, on the other hand, it would not be necessary for the heterogeneous systems, because photogenerated carriers can be accumulated somewhere in the solid. There is an example for the strategy ii) in the literature.¹ Co phosphide of O₂- evolving catalyst reported by Professor Nocera is also one example.²

1 Y. Kuang, Q. Jia, G. Ma, T. Hisatomi, T. Minegishi, H. Nishiyama, M. Nakabayashi, N. Shibata, T. Yamada, A. Kudo and K. Domen, "Ultrastable low-bias water splitting photoanodes *via* photocorrosion inhibition and *in situ* catalyst regeneration", *Nat. Energy*, in press.

2 M. W. Kanan, Y. Surendranath and D. G. Nocera, *Chem. Soc. Rev.*, 2009, 38, 109.

Hyunwoong Park replied: The durability of a material or a system can be enhanced by reducing the light intensity. If the charge transfer is limited under irradiation of a strong light, a fraction of the photogenerated charges should be accumulated (*e.g.*, blue TiO₂ under laser irradiation). This charge accumulation can induce unwanted photoreactions including photocorrosion. If a semiconductor undergoes this kind of surface change, then it can be healed by post-processes such as oxidative (or reductive) annealing. This healing mechanism is rather different from that of natural photosynthesis.

Flavia Cassiola addressed Young Soo Kang and Akihiko Kudo: What are the sources of CO₂ in the systems you are studying at the moment? Has any system been designed to make use of atmospheric CO₂ capture? What would you propose as a hypothetical atmospheric CO₂ capture system, in case you are not considering one, but could have one?

Young Soo Kang responded: Yes, ideally we have to reduce atmospheric CO₂. But in this study we have used CO₂ gas bubbling to illuminate the process as a whole system.

Akihiko Kudo answered: We use 1 atmosphere of CO₂ from a cylinder. We could use such highly concentrated CO₂ from some industries. I have no plans to use atmospheric CO₂ at the moment.

Christopher Windle opened a general discussion of the paper by Elizabeth A. Gibson: In your paper, the dye with one acceptor has a much lower absorption coefficient than the dye with two acceptors. Is this a general trend and if so does the effect cancel out because two acceptors absorb more but, due to the footprint, fewer molecules are absorbed onto the NiO?

Elizabeth Gibson responded: Yes, this is a general trend. There's a nice example of this in a PhD thesis from Licheng Sun's group.¹

The benchmark "P1" dye, which our CAD3 structure is based on, is symmetrical with malonitrile acceptors on each of the two thiophene linkers. "P8" has only one malonitrile, the other thiophene is unsubstituted. P1 has an absorption coefficient of 53781 mol⁻¹ cm⁻¹ whereas P8 has an absorption coefficient approximately half that, 27517 mol⁻¹ cm⁻¹. For those dyes the footprint is quite similar so the absorptivity of the P8-sensitized films is about half that of the P1-sensitized film. The maximum IPCE falls from about 55% for P1 to about 45% for P8 under the same solar cell conditions. In our system the CAD4 dye has a much smaller footprint so three times as much dye can be adsorbed on the surface. That partly compensates for the lower absorption coefficient of CAD4 but the difference is more than 7 times so the IPCE is still a bit lower (38% for CAD4 compared to 45% for CAD3) in these devices. CAD1 and CAD2, which only have one acceptor but have the triphenylamine donor, have absorption coefficients approximately double that of CAD4. The IPCE for CAD 1 was 25% and for CAD2 (which has the largest footprint) was 17%. So we have managed to achieve a better balance with our new anchoring system. The plan now is to co-sensitize NiO with CAD4 and a second dye or catalyst.

1 P. Qin, *The Study of Organic Dyes for p-Type Dye-Sensitized Solar Cells*, PhD thesis, Organic Chemistry, KTH Chemical Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden, 2010.

Alexander Kibler commented: Compared to CAD3|NiO, CAD4|NiO experiences a much faster decay of the charge-separated state. Have you considered that this may be due to interactions between the pyrrole moieties in the solid state layers on the solar cell. It has been recently reported that photoinduced electron transfer can occur from the excited state of a donor pyrrole to the Rydberg orbital on the N atom of an acceptor pyrrole; this interaction is long-lived enough to lead to efficient electron relaxation.¹ How could you investigate whether these interactions are possible in your solid state material and whether this relaxation mechanism is influencing the charge recombination step in CAD4|NiO?

1 S. P. Neville, O. M. Kirkby, N. Kaltsoyannis, G. A. Worth and H. H. Fielding, *Nat. Commun.*, 2016, 7, 11357.

Elizabeth Gibson replied: This is an interesting question. I hadn't previously considered the electronic effects of the pyrrole because the electron withdrawing effect of the two carboxylic acids should be very strong. There is an opportunity for hydrogen bonding between the pyrrole and one of the acids but the proton NMR

shows a very broad NH signal that isn't consistent with this (Fig. S1 in the ESI of our paper). It's quite difficult to probe what exactly is happening at the surface. The IR bands are very broad. The DFT calculations (Fig. S11 in the ESI of our paper) suggest that the electron density moves away from the pyrrole to the indolium acceptor on light absorption so there shouldn't be much electronic overlap with the surface to promote recombination. Having said that, the decay of the charge-separated state is always heterogeneous in our transient absorption spectroscopy experiments which suggests there are several recombination pathways. We should also bear in mind that Fielding's studies were performed under vacuum, where weak interactions dominate the behaviour. Ours are in organic solvent in the presence of molar concentrations of salts. It would be interesting to probe this more. We didn't get any information from vibrational spectroscopy. Pump-probe XPS might be one solution.

Leif Hammarström remarked: The transient spectroscopy result shows a surprising increase in lifetime of the reduced dye when electrolyte is added, which is counter-intuitive. We also observed that effect, but not as much as with your CAD3.

It is reasonable to assume, as you pointed out, that this is because the electrolyte reduces NiO holes in valence bands or traps, so that the recombination is slowed down. But you only gain 10 mV in open circuit voltage compared to CAD4, that appears to have 100- to 1000-fold faster recombination. How have you tried to correlate the results with *e.g.* hole lifetime measurements, or impedance spectroscopy?

Elizabeth Gibson answered: We have looked at the dark current and the charge lifetimes for both dyes and these are provided in Fig. S17 and S19 in the ESI of our paper (reproduced here as Fig. 1 and 2). The 10 mV difference in the V_{OC} is consistent with the difference between the dark current curves and the plots of charge-lifetime *vs.* V_{OC} . So we believe that the combination between the electrolyte and the NiO limits the V_{OC} . However this interaction between the electrolyte and the NiO leads to an increase in the lifetime of the charge-separated state and ultimately increases the IPCE and J_{SC} . So there is a trade-off in the device performance overall. See also Fig. 3.

Richard Cogdell asked: How does your system respond to illumination at different light intensities?

Elizabeth Gibson responded: In terms of efficiency, our devices perform very well at low light intensity. At higher light intensity the efficiency increases and then plateaux. The reason is that the lifetime of the charges increases on decreasing the light intensity (you can see this in Fig. S16 and S17 in the ESI of our paper where each point corresponding to a different charge density arises from a different bias light intensity) so the improvement in voltage outweighs the decrease in photocurrent. At higher light intensities ($\gg 1$ sun) then recombination competes with charge transport (for examples, see ref. 1,2 and references therein). This is slightly more important for NiO compared to TiO₂ because in TiO₂ the transport time increases with light intensity but in NiO it doesn't. Still,

what this means is that you have a very versatile device, particularly for applications in Newcastle!

1 D. Dini *et al.*, *Coord. Chem. Rev.*, 2015, **304–305**, 179–201.

2 F. Odobel *et al.*, *Coord. Chem. Rev.*, 2012, **256**, 2414–2423.

Peter Summers queried: In Fig. 3(b) of your paper, looking at the transient absorption experiments. For the dyes on the p-type semiconductor, do you see any evidence of excited state dye before electron transfer from NiO? How does this compare in general to n-type dye electron injection? For CAD4, there appears to be a very similar band (*ca.* 625 nm) in both CH₂Cl₂ and on NiO; could there be residual excited states in this example?

Elizabeth Gibson replied: In general we do not observe the excited state during our transient absorption experiments of dyes adsorbed on NiO. We infer that, like with TiO₂, charge injection is very fast (<1 ps). However, there are limitations to transient absorption spectroscopy, particularly when studying panchromatic dyes such as these, where the transients overlap and decay rapidly. Fig. S26 in the ESI of our paper (reproduced here as Fig. 4) shows the transient spectra at various time delays. The spectral shape is similar to the solution spectrum but at 700 nm, rather than a bleach there is a broad absorption band which is characteristic for holes in NiO. There is a clear isosbestic point at *ca.* 450 nm which suggests that

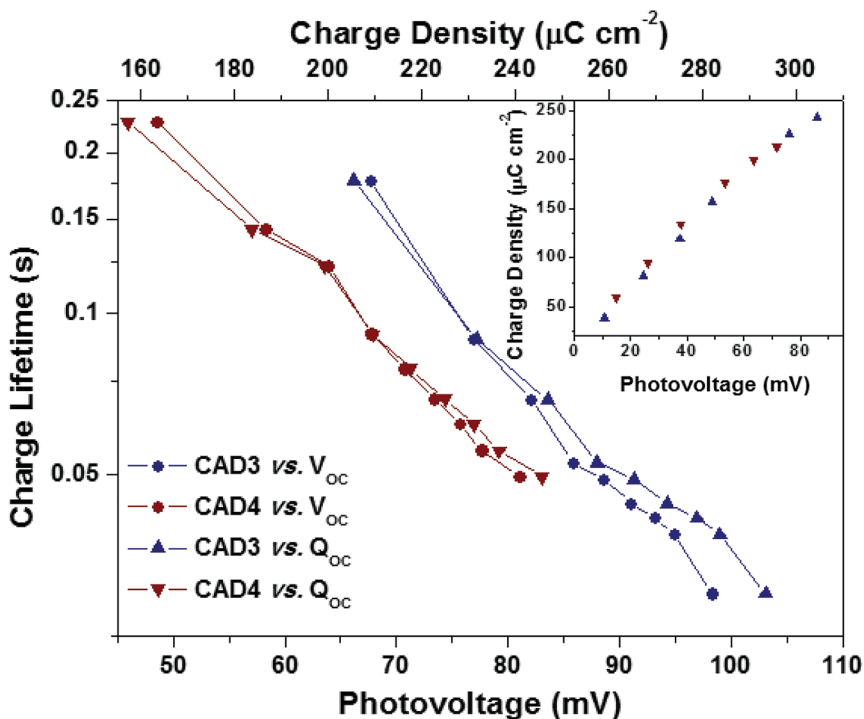


Fig. 1 Charge lifetime vs. photovoltage/extracted charge density and extracted charge density vs. photovoltage (inset) plots for p-DSCs sensitised with CAD3 (blue) and CAD4 (red). Reproduced from Fig. S17 in the ESI of Gibson *et al.* (DOI: 10.1039/c6fd00228e).

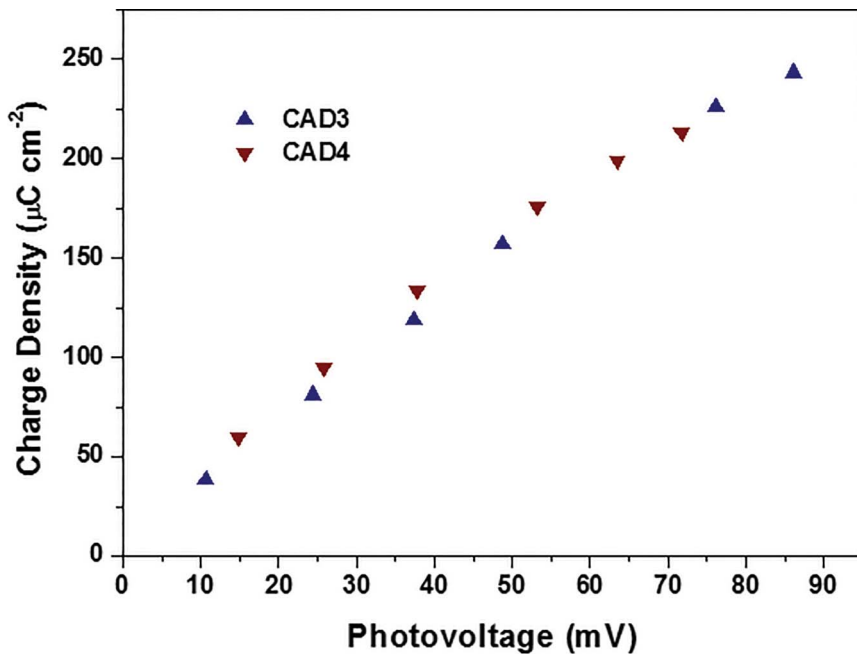


Fig. 2 Extracted charge density vs. photovoltage plot for CAD3 (blue) and CAD4 (red). Reproduced from Fig. S19 in the ESI of Gibson *et al.* (DOI: 10.1039/c6fd00228e).

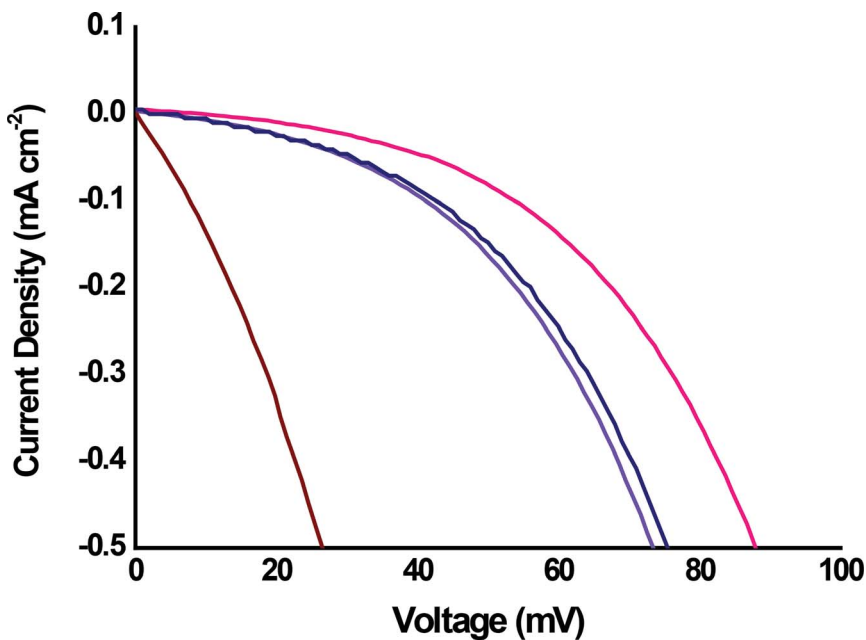


Fig. 3 Dark current curves for CAD4, 2 (pink), 3 (violet) and 4-layered NiO (brown) p-DSCs. The dark current curve for 3-layered CAD2 p-DSCs (blue) has been included for comparison.

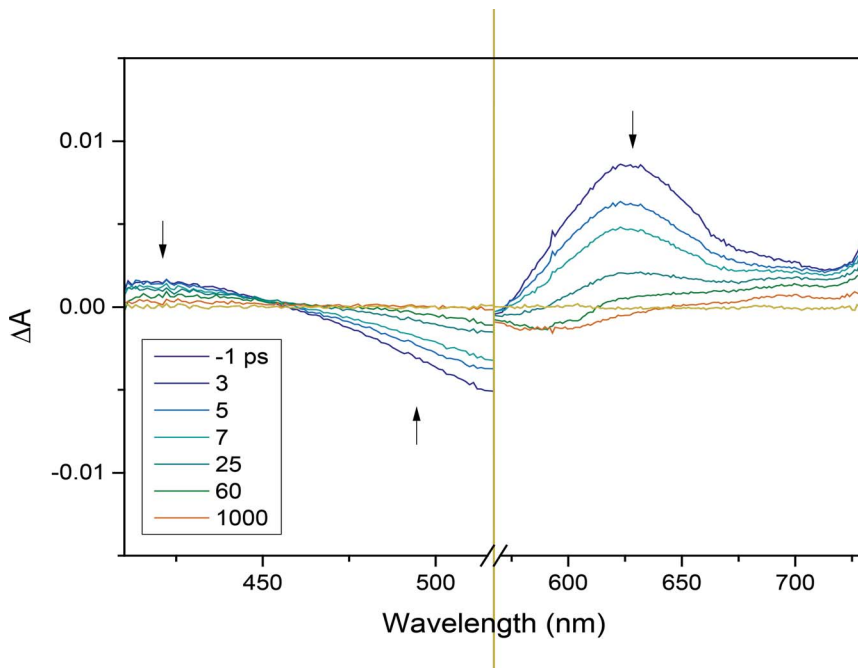


Fig. 4 Transient absorption data for CAD4|NiO at various delay times after excitation at 532 nm. Reproduced from Fig. S26 in the ESI of Gibson *et al.* (DOI: 10.1039/c6fd00228e).

only one species is present. However, we are never completely certain. In our recent study of a dye related to CAD3, but with bodipy as the acceptor rather than indolium, we did observe the excited state as well as the reduced dye. However, in this system the chromophore was electronically decoupled from the triphenyl amine donor. Time-resolved infrared spectroscopy was useful in this case as the transient bands for the donor were very distinctive.¹ We have performed these measurements for CAD3, which were presented in my student's poster, but not for CAD4 (see Fig. 5).

1 F. A. Black, C. A. Clark, G. H. Summers, I. P. Clark, M. Towrie, T. Penfold, M. W. George and E. A. Gibson, Investigating interfacial electron transfer in dye-sensitized NiO using vibrational spectroscopy, *Phys. Chem. Chem. Phys.*, 2017, **19**, 7877–7885.

Devens Gust asked: With these systems, is the most serious charge recombination occurring between the nickel oxide and the reduced sensitizer dye, or between the nickel oxide and the reduced redox relay in solution?

Elizabeth Gibson replied: I believe it's between the charge in the NiO and the redox relay. In the past we thought it was recombination between the dye and the NiO but the effects of the electrolyte on stabilising the charge-separated state weren't taken into account previously.

Devens Gust remarked: In a photoelectrochemical cell for solar fuel production (rather than electricity production), one could slow down charge

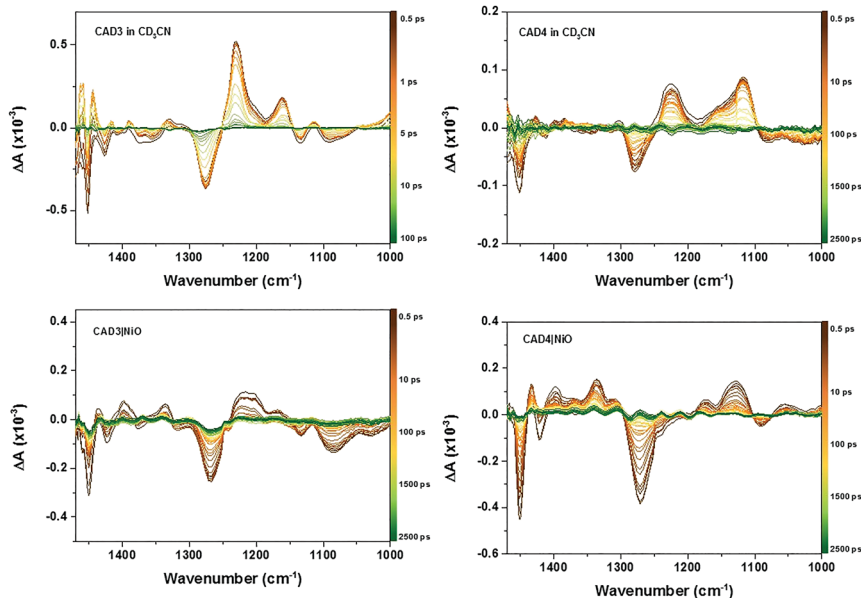


Fig. 5 Time-resolved absorption spectroscopy of CAD3 and CAD4 dyes in CD_3CN solution (top) and adsorbed on NiO (bottom). The excitation wavelength was 532 nm. Experimental details are reported in ref. 1.

recombination by quickly moving an electron from the reduced sensitizer onward to a catalyst. Of course, recombination at other steps would likely still be a problem.

Elizabeth Gibson responded: Absolutely. The challenge is to ensure that charge-transfer to the catalyst proceeds quickly without requiring a large driving force so careful molecular engineering is required. We need to look at the dynamics of dye-sensitized NiO systems in aqueous buffers so we have an idea of where the balance should be. In this system the electrolyte (in acetonitrile) appears to be helping us, but our results so far suggest that that's not the case in water so we need to be smarter.

Leif Hammarström commented: This is a follow-up to Devens Gust's question: you stated that charge recombination between NiO and electrolyte was the main reason for performance loss in the device. What do you base that conclusion on?

We, and the group of Udo Bach, have independently concluded that it is recombination of NiO holes with the reduced dye that is the most important loss, in particular near the maximum power point; we have studied recombination as a function of applied potential.

Elizabeth Gibson responded: Yes, and I admit that we still need to look at the results under applied bias for our system. As far as I'm aware the other studies did not examine the charge-separated state in the presence of the triiodide-iodide electrolyte. Your study and Bach's showed that recombination between charges in the dye and the NiO is accelerated upon increasing positive bias. Bach has shown

that this becomes competitive with dye regeneration (using $[\text{Co}(\text{en})_3]^{3+}$ as the acceptor) on approaching open circuit voltage.¹ However, we have also both shown that the NiO charge lifetime decreases on approaching open circuit until it is competitive with charge transport.² The NiO charge lifetime is also strongly dependent on the electrolyte so the bias at which the recombination limits the charge extraction varies (it is much higher for cobalt electrolytes compared to I_3^-/I^-). For this system the lifetimes are plotted vs. V_{OC} in Fig. 1.

So both recombination processes get faster as the concentration of charge increases (short circuit to open circuit conditions). Which one dominates depends on the dye and the electrolyte. One reason that I believe the dominant recombination reaction is to the redox relay in this system comes from the thickness dependence on the efficiency (see Table 1). As the thickness is increased the J_{SC} improves (because the light harvesting increases) but the V_{OC} decreases (the charges have further to travel, increasing the likelihood of recombination). If recombination with the electrolyte wasn't a problem, the diffusion length would be longer. This is particularly a problem for CAD4 which has a smaller footprint than CAD3. Beyond four layers the decrease in V_{OC} affects the efficiency more than the increase in J_{SC} .

1 S. Powar, T. Daeneke, M. T. Ma, D. Fu, N. W. Duffy, G. Götz, M. Weidener, A. Mishra, P. Bäuerle, L. Spiccia and U. Bach, *Angew. Chem., Int. Ed. Engl.*, 2013, **52**, 602–605.

2 L. Le Pleux, A. L. Smeigh, E. Gibson, Y. Pellegrin, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarström and F. Odobel, *Energy Environ. Sci.*, 2011, **4**, 2075–2084.

Table 1 Photovoltaic performance of 2, 3 and 4-layered NiO p-DSCs incorporating CAD4

Dye / # Layers NiO	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF (%)	η (%)	IPCE (%)
CAD4 / 2 Layers	1.83	90	34	0.056	16
CAD4 / 3 Layers	3.32	80	30.8	0.082	25
CAD4 / 4 Layers	4.25	68	30.6	0.089	38

Leif Hammarström remarked: Maybe you are right that is true for the I_3^-/I^- electrolyte, which can interact with the dye and give ultrafast regeneration (10 ps timescale) – we have seen this in our first studies. But this is not true for most other electrolytes and maybe not all dyes. Maybe your dyes are designed to have a good interaction with the electrolyte, and that is why you have better regeneration?

Elizabeth Gibson responded: Yes, so the difficulty with I_3^-/I^- is that we can't estimate the dye regeneration efficiency because the lifetime of the reduced dye increases in the presence of the redox relay rather than decreases as expected. In Bach's paper¹ there was more than an order of magnitude reduction in lifetime in the presence of $[\text{Co}(\text{en})_3]^{3+}$ compared to the inert electrolyte. In ours there is a factor of 10 increase in the lifetime when I_3^-/I^- is added to the electrolyte, which I believe stems from the I^- reacting with Ni^{3+} . The lifetimes of both CAD4 and CAD3 are both much longer than we observed with neutral dyes [see ref. 2 for example]. Our system is optimised for iodine, whereas theirs is optimised for cobalt. When other electrolytes are used then clearly the dynamics will change and we do find we need a longer-lived charge-separated state for good performance with non-iodine-based relays.

- 1 T. Daeneke, Z. Yu, G. P. Lee, D. Fu, N. W. Duffy, S. Makuta, Y. Tachibana, L. Spiccia, A. Mishra, P. Bäuerle and U. Bach, *Adv. Energy Mater.*, 2015, 5, 1401387.
- 2 F A. Black, C. A. Clark, G. H. Summers, I. P. Clark, M. Towrie, T. Penfold, M. W. George and E. A. Gibson, Investigating interfacial electron transfer in dye-sensitized NiO using vibrational spectroscopy, *Phys. Chem. Chem. Phys.*, 2017, 19, 7877–7885.

Yuki Shinohara opened a discussion of the paper by Rengui Li: Is there any stability difference between impregnated samples and photodeposited samples? Spatial distribution of cocatalysts is also good for stability improvement?

Is there any change between before and after the stability test (morphology change, distribution disorder of cocatalysts, *etc.*)?

Rengui Li replied: Both impregnated and photodeposited samples are quite stable during the photocatalytic hydrogen production experiment for more than 20 h and almost no decrement could be found in our experiment. We also checked the SEM images of Pt-MnO_x/PbTiO₃ after the photocatalytic reaction, and the spatial distribution behavior and morphology of Pt and MnO_x are still maintained without any obvious change.

Hyunwoong Park commented: You show hydrogen production data, and compare the two systems: selective and randomly distributed systems. My concern is how do you control and calculate the same amount of cocatalyst on the surface?

Rengui Li replied: This is a very good question. Actually, we normalized the photoactivity by the surface atoms of cocatalyst. For example, we measured the number of Pt atoms exposed on the outer surface by CO absorption, and assuming only Pt atoms exposed to the outer surface are reaction active sites, the photoactivity on each Pt atom could therefore be calculated. Then we compared the performance of different photocatalysts systems after we normalized the photoactivity.

Hyunwoong Park asked: In both systems, is the same amount of Pt cocatalyst deposited?

Rengui Li responded: Yes, the amount of Pt cocatalyst was confirmed to be comparable by ICP analysis. In addition, we also compared the performance of different photocatalyst systems after normalization by the number of Pt atoms exposed on the outer surface.

Hyunwoong Park queried: After prolonged photocatalysis, what happened to the Pt? Is cocatalyst performance related to catalyst size?

Rengui Li replied: The photocatalyst was stable for more than 20 h during photocatalytic evaluation. After the photocatalytic reaction, we also checked the SEM images of photocatalyst, and we didn't see any obvious change in the photocatalyst and Pt cocatalyst. Actually I strongly believe that the photocatalytic performance is closely related to cocatalyst size, which may have a more remarkable effect for the oxidation cocatalyst. In our future work, we will check the size effect of cocatalysts for photocatalytic overall water splitting.

Akihiko Kudo remarked: You showed a nice picture. What is the origin of the selective deposition of Pt on the lines on the surface as shown in Fig. 2 of your paper?

Masanori Kodera asked a related follow-up question: What is the origin for forming the line shape of the deposited cocatalyst? I'm curious about the direction of electric field. If Pt and MnO_x were deposited alternately, does this mean that the electric field is generated parallel to the surface to assist the charge separation on the surface? Or can this electric field contribute to extract carriers from inside the particle?

Rengui Li responded: Based on our present experimental data and understanding, the selective distribution of cocatalysts on the surface of PbTiO_3 is possible due to its internal ferroelectric field induced by the disorder of its unique perovskite ABO_3 crystal structure. The as-prepared PbTiO_3 particles are composed of some parallel domains with spontaneous polarization; in a specific domain, the electric field could induce the separation of electrons and holes so that the photo-reduction deposition of Pt and photo-oxidation deposition of MnO_x are separated onto different sites. However, we are still working on this system in order to get more direct evidence to support the above prediction. Another experiment that we have done is that when PbTiO_3 was synthesized with a single domain by a hydrothermal method, the deposition of Pt and MnO_x could only be found on the opposite side of a particle, indicating that there exists an electric field between positive and negative sides induced by its ferroelectric properties. The results of line-by-line distribution could be understood by the sum of many cases with single-domain ferroelectric units.

Akihiko Kudo asked: How does the ferroelectric property bring such selective deposition of Pt? Is the place of the selective deposition a kind of boundary exposed to the surface? Dr Inoue from Nagaoka University of Technology has reported the enhanced charge separation by the dielectric property of photocatalysts.¹

1 Y. Inoue, *Energy Environ. Sci.*, 2009, 2, 364.

Rengui Li responded: Thanks for your questions and comments. In my opinion, the as-prepared PbTiO_3 is a multi-domain containing particle, and the boundary of different domains prefers to accumulate photogenerated charges induced by a ferroelectric field. Dr Inoue also discussed the relationship between ferroelectric field induced charge separation and photoactivity for many kinds of typical photocatalysts in the above mentioned paper, which is really instructive for constructing a ferroelectric photocatalyst for solar water splitting and understanding the mechanism of the ferroelectric effect on photogenerated charge separation.

Masanori Kodera asked: Have you ever tried the overall water splitting reaction? Moreover, how about the case of the oxygen evolution reaction? The reason the MnO_x cocatalyst for oxygen evolution improves the hydrogen evolution reaction seems unclear.

Rengui Li replied: Yes, the overall water splitting on Pt–MnO_x/PbTiO₃ photocatalyst has been checked in our experiment and unfortunately, we failed to achieve it. But both hydrogen production and oxygen production half reactions can be successfully achieved in the presence of sacrificial reagents. In my opinion, the improvement of hydrogen production after MnO_x deposition is due to the enhancement of the CH₃OH oxidation half reaction so that the hydrogen production activity is improved.

Akira Yamakata queried: Why is Pt deposited as a "line-shape"? I think there are many steps on the crystals. Is there any relationship with the steps of the crystals ?

Akihiko Kudo asked a related follow-up question: Is the place of the selective deposition on some specific surface such as a nano-step structure? We have also observed such selective deposition of Pt on AgInS₂–ZnS photocatalysts. In this case, Pt was deposited on the edge of a surface nano-step structure.

1 I. Tsuji, H. Kato, H. Kobayashi and A. Kudo, *J. Am. Chem. Soc.*, 2004, **126**, 13406.

Rengui Li responded: We have checked the deposition behavior of Pt and Au particles on PbTiO₃ with a nano-step structure on the surface, as shown in Fig. 6. It could be distinctly observed that the photo-deposition still follows the regular pattern but takes place at the nano-step site, implying that the spatial charge separation on PbTiO₃ particles is not related to its step-like surface morphologies. In our case, it is different from the selective deposition of Pt on the nano-step of AgInS₂–ZnS photocatalysts.

Akira Yamakata asked: Pt is loaded as a "line-shape", but MnO_x is not a "line". MnO_x seems to be loaded on the "terrace" of the crystals. When Pt and MnO_x are co-loaded, MnO_x becomes "line-shape". Can you tell me why the structure of loaded MnO_x changes ? The shape of the loaded Pt and MnO_x is very interesting, but what is the driving force that determines the structure of loaded Pt and MnO_x?

Rengui Li replied: This is also an interesting question that puzzled me a lot. A possible explanation is that after the initial deposition of Pt or MnO_x particles on the surface of the PbTiO₃ photocatalyst, a junction is formed at the interface between cocatalyst and PbTiO₃, which may slightly change the built-in electric field in the bulk of the photocatalyst and consequently leads to the slight change of surface charge distribution under illumination. However, we don't have direct evidence at the moment. Further characterization is needed to investigate it.

Akihiko Kudo asked: In your case, the selective deposition is not on a step, but on a line perpendicular to step structure. Is it correct?

Rengui Li replied: As we can see from Fig. 6 above, the photo-deposition of Pt is not correlated to the surface step-like structure, neither parallel nor perpendicular to the surface step of PbTiO₃.

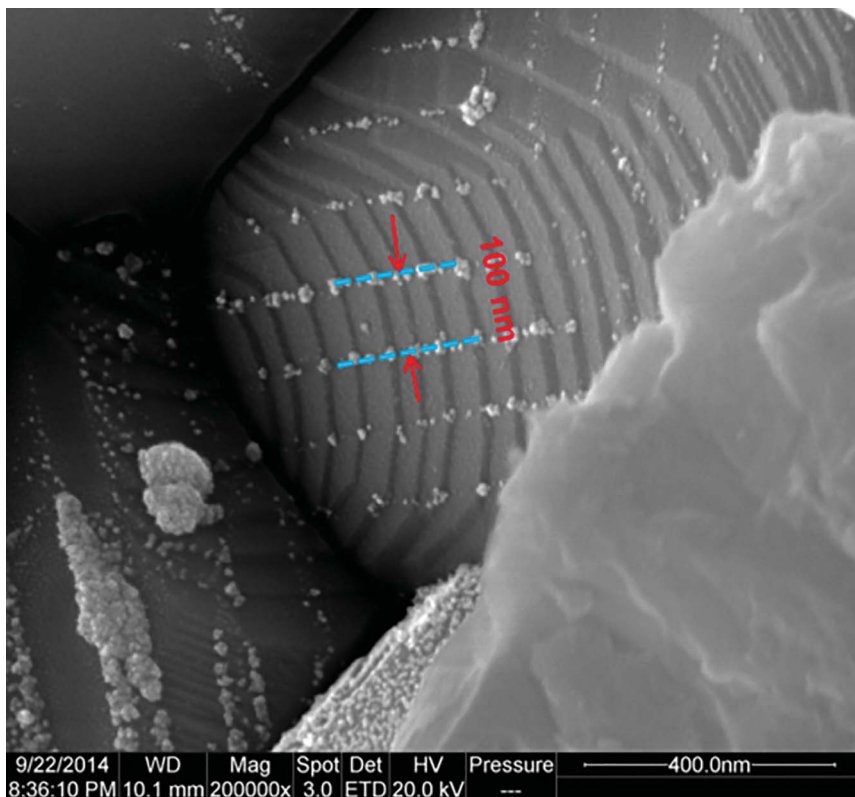


Fig. 6 SEM image of photo-reduction deposition of Pt nanoparticles on PbTiO_3 crystals with step-like structure on the surface. Reproduced from Fig. S2 in the ESI of Li *et al.* (DOI: 10.1039/c6fd00199h).

Masanori Kodera opened a discussion of the paper by Fengtao Fan: In SPS measurements, light intensity is important. Did you observe any light intensity dependence in your experiment? In other words, in a real situation where the photocatalytic reaction proceeds, is the potential difference between two facets still 25 mV or larger under AM 1.5G sunlight irradiation?

Fengtao Fan responded: The light intensity will truly affect the measured potential difference. In our experiment, the light intensity was optimized so that we can provide a saturated Surface Photovoltage (SPV) signal, which can reflect the driving force for the charge separation.

Akihiko Kudo said: This kind of measurement is very important to get fundamental information. There may be a thermal effect in such a measurement because the temperature of the sample may increase with light irradiation. How can the thermal effect be excluded?

Fengtao Fan answered: We used modulated light and a lock-in amplifier to obtain the potential changes between light on and off. The method is quite

reliable because the short time constant (typically 6 Hz) means the thermal effect can be excluded.

Akira Yamakata commented: I am interested in the uniformity of the loaded cocatalysts on the facets. The cocatalysts are loaded uniformly on some facets, but not uniform on several facets. I wonder if the surface structure of the facets affects the photocatalytic reactions for the deposition of the cocatalysts. I agree that the accumulation of electrons and holes depends on the facets *via* the built-in electric field, but the surface structure would also be important for the chemical reactions. The uniformity of the loaded cocatalysts would be supporting the structure-dependent reactions.

Fengtao Fan replied: The cocatalysts are loaded in a highly isolated fashion and some of them are non-uniformly distributed on the 010 facet. However, the relatively low resolution of KPFM (about 40 nm) can not distinguish the changes in the built-in electric field just beneath the cocatalyst.

Elizabeth Gibson remarked: You have shown a beautiful technique for studying very large crystals. What about very small ones, *e.g.*, nanoparticulate crystals, especially less than 100 nm, which is typical for many water splitting systems. How are you approaching this problem and how do your results relate to photocatalysis in these systems?

Fengtao Fan responded: The sizes of the crystal will have a significant impact on the charge separation due to the relaxation of the space charge region. The smaller crystal will be in favor of the connection of the space charge region from facet to facet and thus results in the efficient charge separation between different places on the surface of the catalyst. However, a crystal size smaller than the space charge region will lead to decreased charge separation efficiency due to the unrelaxed depletion region.

Can Li returned to the discussion of the paper by Elizabeth Gibson: The DSSC system is very different from photocatalysis. How much contribution comes from the charge separation in your system using NiO?

Elizabeth Gibson replied: Charge separation is fundamental in both DSSCs and dye-sensitized photoelectrochemical water splitting cells. The initial charge-separation step (charge injection) appears to be rapid (<ps), which is similar to TiO₂ DSSCs. However, the IPCE (EQE) depends on the charge-separation efficiency and it is only 50–60% in our NiO DSSCs compared to at least 80% in TiO₂ DSSCs. Currently, when we switch to hydrogen evolution (in aqueous electrolyte) it falls to <10% which suggests that charge-recombination is a problem for us. I believe that we can learn a great deal from DSSCs that we can apply to photoelectrocatalysis. For example, in DSSCs the redox chemistry of the electrolyte is typically a one electron or two electron process. *ca.* 0.5 V is wasted during dye regeneration either at a photocathode (NiO) or photoanode (TiO₂) when I₃⁻/I⁻ is used because the photochemistry driven by the dye is a single electron-transfer reaction. The radical species (I₂⁻) generated then undergoes disproportionation. The dark catalytic reaction at the Pt counter electrode is a two electron

process. If we are to produce H_2 (2 electrons) or O_2 (4 electrons) efficiently, we need to be much smarter about coupling the photochemistry to the catalysis. The charge-separated states need to be very long lived to cope with the low photon flux, and/or we need to be able to funnel the charge to the catalyst rapidly.

Young Soo Kang addressed Rengui Li: I am concerned about crystal engineering. Even if you add some kind of cocatalyst, the aspect ratio of the crystal is very important. The 010 surface area compared to the others is very important. How do you control the charge separation efficiency by controlling the difference in the ratio?

Rengui Li responded: As spatial charge separation takes place between different facets, the charge separation efficiency is closely related to the ratio of exposed facets for the reduction reaction and oxidation reactions. In the case of BiVO_4 , the {010} facet is available for the reduction reaction and the {110} facet for the oxidation reaction. Both facets provide the active sites for reduction and oxidation facets, respectively. Therefore, the ratio of {010} and {110} should be optimized for the best charge separation efficiency and surface catalytic reactions. We can rationally control the ratio of {010} and {110} facets for BiVO_4 crystals from nearly 100% to less than 10% in our recent work *via* controlling the conditions of the hydrothermal process to optimize the best photocatalyst.

Young Soo Kang asked: Have you tried to get the efficiency of aspect ratio to have some kind of hydrogen production? Different crystals should have different abilities. Even if you have a 1 to 1 aspect ratio, you should get a different efficiency.

Rengui Li replied: We have tried to concisely control the preparation conditions for photocatalysts with different exposed facets to make sure that the result is comparable enough, however, we still need more direct evidence to demonstrate that the different photoactivity is really due to different functioned facets.

Licheng Sun opened a general discussion of the papers by Elizabeth Gibson, Rengui Li and Fengtao Fan: Regarding the common use of a p-type material for hydrogen production – do you think Ni oxide is an ideal material or should we look at others?

Elizabeth Gibson responded: So far there has not been a transparent p-type material that has performed better than NiO. In fact, we were very surprised that our photocathodes show excellent stability during photocatalysis under aqueous conditions. This, together with the very straightforward synthesis of the material means it continues to be the first choice of most researchers in this area. Nonetheless, there are problems, such as fast charge-recombination and the relatively high valence band energy. The focus of my research group now is to develop alternatives to NiO and in a few years time we will be able to reflect on this question in context.

Haruo Inoue addressed Rengui Li and Fengtao Fan: It is very interesting to see the beautiful line-shaped alignment of the deposited Pt and MnO_2 on the ferroelectric PbTiO_3 . You mentioned that the reactivity of H_2 evolution is 15 times more

efficient on the ferroelectric semiconductor owing to the built-in electric field than the ordinary one. But may I ask about the microscopic potential bending of the conduction band? Supposing the built-in electric field enhances the charge separation, it means that the excited electron in the conduction band is repelled from the negatively charged site or attracted by the positively charged site. The electron may then lose its potential by sliding down from the negatively charged site to the positively charged site, even when the overall Fermi level is unchanged. Even in this case, the reactivity is enhanced. How can we understand it?

Rengui Li replied: Thanks for your good question. The polarization in ferroelectric semiconductors should lead to band bending at the surface that promotes the transfer of charge to the adsorbed species. PbTiO_3 is an n-type semiconductor and the band bending at the interface of semiconductor/solution is upward. It is right that the excited electron in the conduction band is attracted by the positively charged site and the electron may lose its potential by sliding down from the negatively charged site to the positively charged site. However, this situation will be changed after the cocatalysts are deposited, because when the cocatalyst is deposited on the surface of a photocatalyst, a depletion layer is formed at the interface between cocatalyst and photocatalyst and a built-in electric field induced by the depletion layer also induces the charge separation and charge transfer. The built-in electric field at the interface and the synergistic effect of Pt and MnO_x cocatalysts together contributes to the surface reduction and oxidation reactions.

Fengtao Fan responded: The resulting built-in electric field will truly affect the energy of the carriers including the electrons. However, the minimum energy of the electron will be restricted by the CBM. In this case, the reactivity will be affected by the numbers of the separated photogenerated carriers rather than their potential energy

Haruo Inoue addressed Fengtao Fan: You showed that the difference in the potential between different facets is in the order of several tens of millivolts; that is a big difference. Does the electron slide down to lose its reducing power?

Fengtao Fan replied: The potential differences on the surface of the crystal are reflecting the difference of the surface work functions of the material. The resulting built-in electric field will truly affect the energy of the carriers including the electrons.

Can Li asked a general question: Molecular catalysts, solid catalysts and their interface between the catalysts and semiconductor have been the problem for many years, and the charge transfer from semiconductor to dye have been discussed intensively. What is the general conclusion for charge transfer in these systems, and what is the key factor determining the efficiency of charge transfer?

Elizabeth Gibson responded: I believe that despite the intensity of research in this area, much is still not known as many of these studies were conducted in the absence of the electrolyte. What I've attempted to demonstrate in our paper is that the electrolyte composition is extremely important and now our research

must focus on studying the impact that the environment has on charge-separation. Recently we found that simply using transient absorption spectroscopy wasn't sufficient as transients with strong absorption coefficients can mask transients with weaker signals. Furthermore, if the decay of the transient is on a similar timescale to the formation then the kinetics are skewed. That said, the key factors are still those in Marcus's equation. We need strong electronic coupling in the ground state, suitable driving force *etc.* Generally the consensus is that for NiO a charge-transfer excited state gives the best performance. Push-pull systems or electron transfer to secondary acceptors lengthens the charge-separated state. For NiO we observe a considerable minimum driving force for electron transfer to the dye so we need to understand which states the dye must couple to in order for us to improve the efficiency further.

Flavia Cassiola addressed Elizabeth Gibson: You commented that instruments are not sophisticated enough. What is missing? Should we be looking at other disciplines and their instrumentation, or perhaps the way techniques are explored in other disciplines? What should we be using that we are not using currently?

Elizabeth Gibson replied: The challenge is that photoelectrochemical systems are very complicated. I believe that we are limited by current instrumentation to investigating model systems and those which suit our particular technique. It's often very difficult to decouple the effect of one variable from another. It's also very difficult to look at the interfaces between the different components in our devices under operational conditions. For example, most surface-sensitive techniques are performed under vacuum and so they neglect the effect of the electrolyte, which, as I have shown here, can be very important. We've been fortunate that in many photoelectrochemical systems you can frequency resolve the different steps in the mechanism so that allows you to probe different steps at different timescales. However, as we optimise the system, the differences may shorten as we strive towards higher efficiency. Transient optical spectroscopy becomes less valuable when panchromatic absorbers are used (required for good light harvesting) and the transients overlap in the same region of the spectrum. We are getting around this by applying more techniques in parallel. It's also important to study the best quality devices or materials as possible. Often the labs which have the specialist equipment are not the labs which make the best devices and so incorrect assumptions can be made about what is really limiting the device. I think there are good examples of this in the PV (especially perovskite solar cell) community. So certainly we should be collaborating more and I know that there are new developments in low pressure X-ray techniques which we haven't exploited yet. We should look more at the techniques used in the battery and heterogeneous catalysis fields. But I think fundamentally it is always going to be a challenge to come up with state-of-the-art techniques to increase our understanding of the fundamental chemistry in complete devices.