

Photo-recycling the Sacrificial Electron Donor: Towards Sustainable Hydrogen Evolution in a Biphasic System

Peiyu Ge,^[a] Mohamad Hojeij,^[a] Micheál D. Scanlon,^{[b,c]*} and Hubert H. Girault^{[a]*}

[a] Laboratoire d'Électrochimie Physique et Analytique. École Polytechnique Fédérale de Lausanne, EPFL, Valais Wallis Rue de l'industrie, 17, 1950 Sion (Switzerland)

[b] The Bernal Institute and Department of Chemical Sciences, University of Limerick (UL) Limerick V94 T9PX, Ireland.

[c] Marine and Renewable Energy Ireland (MaREI) centre

Corresponding authors:

*E-mail: micheal.scanlon@ul.ie

*E-mail: hubert.girault@epfl.ch

Abstract

H₂ may be evolved biphasically using a polarised liquid|liquid interface, acting as a “proton pump”, in combination with organic soluble metallocenes as electron donors. Sustainable H₂ production requires methodologies to recycle the oxidised donor. Herein, the photo-recycling of decamethylferrocenium cations (DcMFC⁺) using aqueous core-shell semiconductor CdSe@CdS nanoparticles is presented. Negative polarisation of the liquid|liquid interface is required to extract DcMFC⁺ to the aqueous phase. This facilitates the efficient capture of electrons by DcMFC⁺ on the surface of the photo-excited CdSe@CdS nanoparticles, with hydrophobic DcMFC subsequently partitioning back to the organic phase and resetting the system. TiO₂ (P25) and CdSe semiconductor nanoparticles failed to recycle DcMFC⁺ due to their lower conduction band energy levels. During photo-recycling, CdS (on CdSe) may be self-oxidised and photo-corrode, instead of water acting as the hole scavenger.

The development of strategies to overcome the intermittent nature of renewable energy production from wind or solar is of paramount importance to realise a future powered by clean energy.^[1] For long-term energy storage, trapping the renewable energy in the form of chemicals, such as molecular hydrogen (H₂), will allow stockpiling of clean energy produced in excess.^[2] The solar fuel may then be consumed on demand. H₂ can be readily obtained in

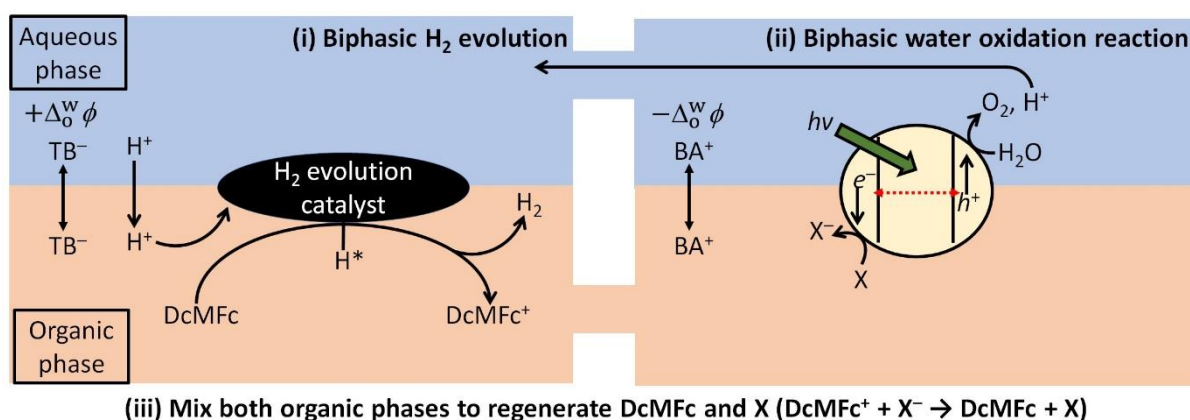
large amounts by splitting water and, thus, the development of efficient and sustainable methods to produce H₂ by water splitting is the focus of intense research efforts.^[3]

Certain interfaces between two immiscible electrolyte solutions (ITIES) may be polarised positively or negatively either externally using a potentiostat or chemically by partition of a common ion between the phases.^[4] Partition of the lipophilic tetrakis(pentafluorophenyl)borate anion (TB[−]) will polarise the interface positively, producing an interfacial Galvani potential difference ($\Delta_0^w \phi$) of +0.58 V. However, partition of the lipophilic bis(triphenylphosphoranylidene)ammonium cation (BA⁺) will polarise the interface negatively ($\Delta_0^w \phi = -0.60$ V).^[5] A positively polarised ITIES can act as a “proton pump”, with protons either directly transferring from the aqueous to organic phase or undergoing facilitated ion transfer (FIT) by interfacial complexation with a suitable lipophilic molecule.

Organic soluble metallocenes form hydride species by a FIT mechanism and are capable of evolving H₂ by acting as the electron donor either spontaneously in the dark, *e.g.*, decamethylferrocene (DcMFc),^[6] or by photo-exciting the hydride species, *e.g.*, osmocene (Oc),^[7] decamethylosmocene (DcMOc)^[8] or decamethylruthenocene (DcMRu).^[9] The kinetics of the “dark” biphasic HER may be enhanced by floating interfacial H₂ evolution catalysts in a process known as interfacial redox electrocatalysis.^[10] Besides H₂, the other by-product of the dark or photo-driven biphasic HER is the oxidised metallocenium cation, *i.e.*, DcMFc⁺ or DcMRu⁺. If the latter remains oxidised, this means that a fuel (the metallocene) is consumed to produce H₂. Such a sacrificial system is not sustainable and, thus, strategies must be developed to close the loop and recycle, *i.e.*, reduce, the metallocenium cation using a renewable source of electrons for continuous H₂ evolution.

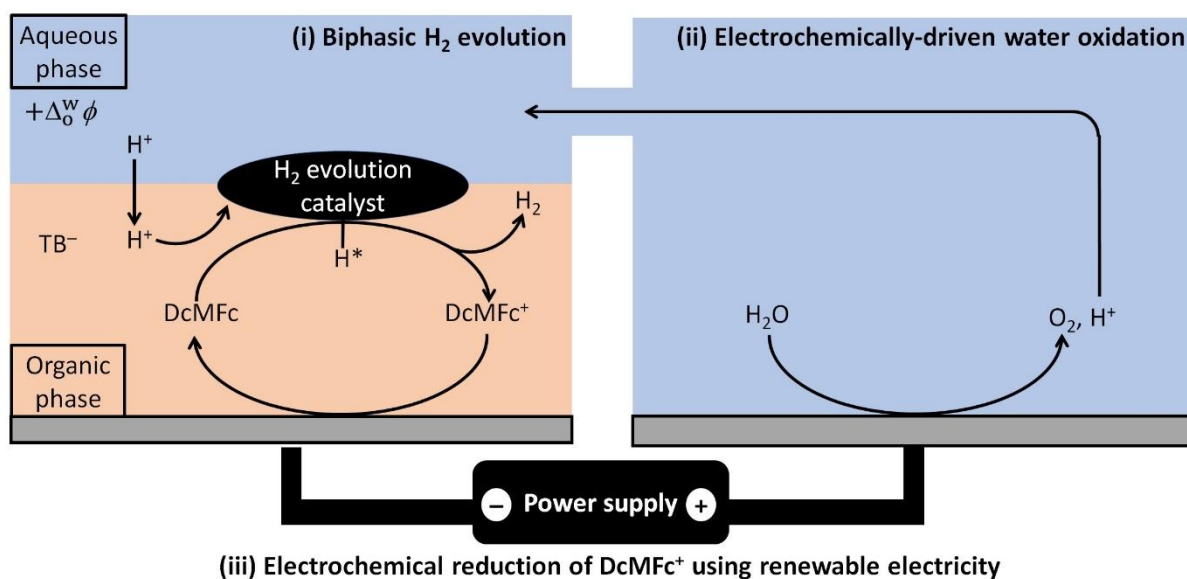
Whereas DcMFc⁺ is a stable species in the organic phase, thereby enhancing its recyclability, DcMRu⁺ is typically not stable with a very short lifetime under photo-illumination. However, in breakthrough studies, the use of a non-coordinating organic solvent (1,2-dichloroethane, DCE) and non-nucleophilic organic anion (TB[−]) was found to stabilise DcMRu⁺ long enough to permit its electrochemical regeneration both in a single organic phase^[11,12] or biphasic system.^[13] The major advantage of using photo-excited metallocenes is their higher (more positive) redox potentials in comparison to DcMFc.^[14] Thus, DcMRu⁺ may be recycled more easily than DcMFc⁺, using weaker chemical reductants or at more positive electrode potentials.

One closed loop strategy to generate H_2 sustainably is the concept of biphasic “batch” water-splitting whereby the metallocenium cation may be recycled by a reduced lipophilic species (X^-) sourced from a second half-reaction, ideally the light-driven water oxidation reaction (WOR) at a negatively polarised ITIES.^[15] The latter half-reaction has been demonstrated experimentally by Rastgar and Wittstock using a semiconductor-functionalised ITIES.^[16–18] In theory, both half-reactions will be “reset” by mixing the organic phases after photoirradiation ($\text{DcMFC}^+ + \text{X}^- \rightarrow \text{DcMFC} + \text{X}$), see Scheme 1.



Scheme 1. Biphasic “batch” water splitting. (i) During biphasic H_2 evolution, the ITIES is polarised positively by distribution of lipophilic TB^- to drive protons to the organic phase. The dark HER depicted using DcMFC can be replaced with a photo-driven HER using DcMRu in an alternative configuration. (ii) During the biphasic water oxidation reaction, the ITIES is polarised negatively by distribution of lipophilic BA^+ to minimise electron (e^-)-hole (h^+) recombination in the semiconductor under photo-illumination, driving holes to the aqueous phase to oxidise water and electrons to the oil phase to reduce a lipophilic redox species (X/X^- , e.g., $[\text{Co}(\text{bpy})_3]^{3+/2+}$). (iii) Subsequent mixing of the organic phases can regenerate the electron donor (DcMFC) and electron acceptor (X) spontaneously based on their redox potentials, resetting both half-reactions.

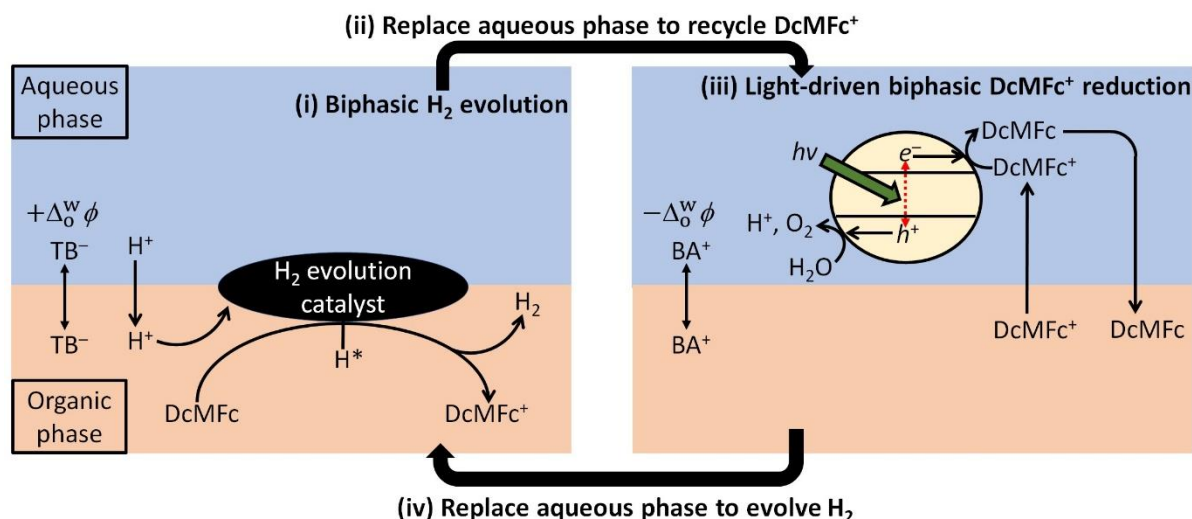
A second closed loop strategy is to electrochemically reduce the metallocenium cation at an electrode surface using electricity produced renewably by wind, solar, hydro, *etc.* A biphasic electrolysis H-cell configuration was designed to demonstrate this concept with DcMFC, see Scheme 2.^[19]



Scheme 2. A biphasic electrolysis H-cell. (i) During biphasic H_2 evolution, initially the organic phase is prepared with just the oxidised DcMFC^+ present (as a $\text{DcMFC}^+\text{TB}^-$ salt). Reduction of DcMFC^+ at the electrode polarises the ITIES positively and protons are pumped to the organic phase to maintain electroneutrality. The choice of organic electrolyte anion is crucial; the organic anion must be very lipophilic such that protons preferentially transfer to the aqueous phase rather than the organic anion transferring to the aqueous phase.^[19] The dark HER depicted using DcMFC can be replaced with a photo-driven HER using DcMRu in an alternative configuration. (ii) The single-phase dark water oxidation reaction can be replaced with a biphasic light-driven water oxidation reaction, as depicted in Scheme 1(ii), in an alternative configuration.^[19] In this case, the lipophilic redox species X^- is oxidised at the electrode surface, see ref. ^[19] for more details. (iii) The potential required to pump electrons from the anodic to cathodic compartments is provided by renewable power sources (wind, solar hydro, *etc.*).

In this Communication, we introduce another closed loop strategy to photo-recycle the metallocenium cation after biphasic H_2 evolution. The concept is illustrated in Scheme 3 using DcMFC . The first step involves contacting an acidified aqueous phase containing LiTB and H_2 evolution catalyst micro/nano-particles with an organic phase containing DcMFC . On contact with the organic phase, TB^- partitions between the phases and polarises the ITIES positively. This leads to protons being pumped to the organic phase, H_2 being evolved and DcMFC^+ produced. The second step involves replacing the aqueous phase with a solution containing semiconductor nanoparticles and a chloride salt of the hydrophobic BA^+ cation. On contact with the organic phase, BA^+ partitions between the phases and polarises the ITIES negatively. The latter induces the extraction of any cations to the aqueous phase with formal ion transfer potentials more positive than -0.6 V. In this regard, DcMFC^+ has a formal ion transfer potential of -0.26 V at the water|DCE interface and is efficiently extracted to the aqueous phase.^[20] In the third step, under photo-illumination, the conduction band electrons reduce DcMFC^+ to

DcMFC, with the valence band holes scavenged to oxidise water. Subsequently, the neutral, hydrophobic DcMFC species partitions back to the organic phase. After a certain time under photo-illumination, the majority of the DcMFC^+ is recycled and finally the aqueous phase is once more replaced with an acidified solution containing the lithium salt of TB^- and a H_2 evolution catalyst to elicit kinetically rapid biphasic H_2 evolution.



Scheme 3. Photo-recycling the metallocenium cation. (i) The dark HER depicted using DcMFC can be replaced with a photo-driven HER using DcMRu in an alternative configuration. (ii) The aqueous phase is replaced with a fresh solution containing semiconductor nanoparticles and BACl. (iii) The negatively polarised ITIES by BA^+ partition induces DcMFC^+ ion transfer to the aqueous phase, where upon photo-illumination it is reduced by the conduction band electrons to DcMFC and subsequently partitions back to the organic phase. (iv) The aqueous phase is replaced again with a fresh solution containing LiTB and a H_2 evolution catalyst.

In order to demonstrate the viability of this concept, three semiconductor nanoparticles were investigated; TiO_2 (P25), CdSe and core-shell CdSe@CdS nanoparticles. Firstly, the biphasic HER with DcMFC catalysed by molybdenum disulphide (MoS_2) particles was performed under anaerobic conditions in a quartz cell for 2.5 hours, as described in numerous previous articles^[21–23] and detailed in the Supporting Information, SI. H_2 evolved was detected by gas chromatography (GC) and the conversion of DcMFC ($\lambda_{\text{max.}} = 425 \text{ nm}$, yellow solution) to DcMFC^+ ($\lambda_{\text{max.}} = 779 \text{ nm}$, green solution) was confirmed quantitatively by UV/vis spectroscopy (and qualitatively by eye). Next, the aqueous phase was replaced by aqueous solutions containing (i) 50% (v/v) CdSe (ii) 50% (v/v) TiO_2 (0.1g/L), and (iii) 25% (v/v) CdSe@CdS nanoparticles, each with 10 mM BACl (Figure 1). In each case, DcMFC^+ was extracted from the DCE phase as indicated by the characteristic green colour of the top (lower

density) aqueous phase, Figures 1(a), (c) and (e), and confirmed by UV/vis spectroscopy, Figure 1(g). In Figures 1(a) and (c), after DcMFC^+ extraction the DCE phase remained yellow due to the presence of unreacted DcMFC from the initial biphasic HER step. Subsequently, each biphasic cell was illuminated using a Xe lamp for 2.5 hours, Figures 1(b), (d), and (f). The use of TiO_2 and CdSe nanoparticles to recycle DcMFC^+ was ineffective, with the DCE phase becoming entirely transparent and the intensity of the green colour of the aqueous phase increasing. This implied that unreacted DcMFC in the DCE phase reacted further to form DcMFC^+ , which transferred to the aqueous phase. Interestingly, when core-shell CdSe@CdS nanoparticles were used, the concentration of DcMFC^+ in the aqueous phase decreased, with the green color of the aqueous phase in Figure 1(f) noticeably lightening and the intensity of the absorbance peak at 779 nm decreasing. The DCE phase became yellow in colour and an absorbance peak at 425 nm appeared, characteristic of the presence of DcMFC , see Figure 1(h). Based on the loss in intensity of the absorbance peak at 779 nm in the aqueous phase, approximately 90% of the DcMFC^+ was recycled under white light illumination indicating an efficient process. Thus, by using solar energy to reset the system, the recycled DcMFC in the DCE phase is now available once more to participate in the biphasic HER.

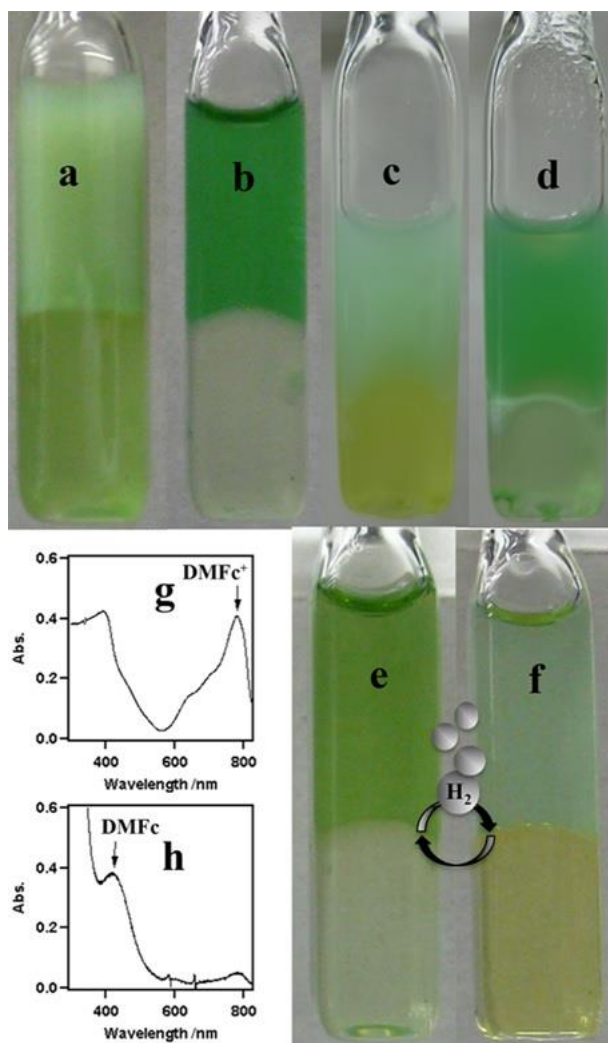


Figure 1. Photographic and UV/vis spectroscopic demonstration of the concept of photo-recycling of DcMFC^+ (produced by the biphasic H_2 evolution reaction, see SI) in the presence of aqueous semiconductor nanoparticles and a negatively polarised ITIES. Experiments with (a, b) CdSe, (c, d) TiO_2 (P25) and (e, f) CdSe@CdS nanoparticles before and after photo-illumination. In each biphasic cell was 5 mM DcMFC^+ , initially in the DCE phase, and 10 mM BACl, initially in the aqueous phase. All experiments were performed under anaerobic conditions and each cell was photo-illuminated for 2.5 hours. (g) UV/vis spectrum of the aqueous phase of (e). (h) UV/vis spectrum of the organic phase of (f).

The ability of the CdSe@CdS nanoparticles to reduce DcMFC^+ in the aqueous phase was due to the more reductive conduction band energy of the CdS shell in comparison with the TiO_2 (P25) or CdSe nanoparticles.^[24] Analysis of the headspace of the biphasic cell with CdSe@CdS nanoparticles present by GC indicated that O_2 was not evolved during the photo-reaction. Thus, the valence band holes were not scavenged by water. The absence of water oxidation may be explained by another well-documented photocorrosion reaction,^[24] described in Equation (1):



To prevent this photocorrosion reaction, another aqueous soluble hole scavenger may be introduced to the system, *e.g.*, an alcohol or S^{2-} . However, this would require re-introducing a sacrificial donor to the biphasic system. Therefore, further explorations with alternative semiconductor nanoparticles with similar conduction band energy levels to CdS is preferable (*e.g.*, CdTe, ZnS, or Sb_2S_3 nanoparticles).^[25]

Control experiments with each of the three nanoparticles to recycle $DcMFe^+$ in the absence of BA^+ partitioning and the associated negative polarisation of the ITIES were unsuccessful, even with CdSe@CdS nanoparticles, as described in the SI. This is ascribed to the lack of physical contact between $DcMFe^+$, which remains trapped in the bulk organic phase at open-circuit potential (OCP) conditions, and the CdSe@CdS which are primarily in the bulk aqueous phase. The concentrations of $DcMFe^+$ and CdSe@CdS in contact at the water|DCE interface are too low to achieve noticeable recycling of $DcMFe^+$.

In this work, we demonstrate the viability of the concept of photo-recycling decamethylferrocenium cations ($DcMFe^+$) using aqueous core-shell CdSe@CdS semiconductor nanoparticles to generate H_2 continuously and sustainably. As this biphasic approach involves alternating between aqueous phases containing H_2 evolution catalysts and LiTB (to evolve H_2) and semiconductor nanoparticles and BACl (to photo-recycle $DcMFe^+$), the chemistry described herein should be integrated in a flow cell to seamlessly flow in-and-out the alternate aqueous phases when required.

Acknowledgements

M.D.S. acknowledges the Science Foundation Ireland (SFI) under Grant No. 13/SIRG/2137 and the European Research Council through a Starting Grant (Agreement No. 716792).

Keywords

Liquid|liquid interfaces • hydrogen evolution reaction • metallocenes • sacrificial electron donor • CdSe@CdS nanoparticles

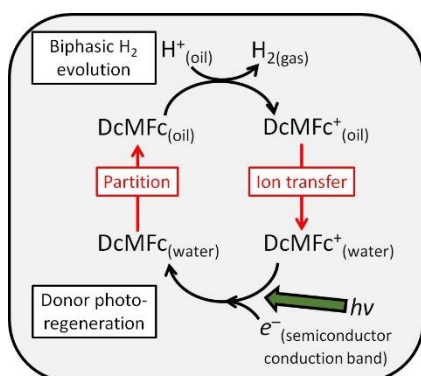
References

- [1] G. Notton, M. L. Nivet, C. Voyant, C. Paoli, C. Darras, F. Motte, A. Fouilloy, *Renew. Sustain. Energy Rev.* **2018**, 87, 96–105.
- [2] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci.* **2006**, 103, 15729–15735.
- [3] S. E. Hosseini, M. A. Wahid, *Int. J. Energy Res.* **2020**, 44, 4110–4131.

- [4] P. Peljo, H. H. Girault, in *Encycl. Anal. Chem.*, John Wiley & Sons, Ltd, Chichester, UK, **2012**.
- [5] B. Su, R. P. Nia, F. Li, M. Hojeij, M. Prudent, C. Corminboeuf, Z. Samec, H. H. Girault, *Angew. Chemie - Int. Ed.* **2008**, *47*, 4675–4678.
- [6] I. Hatay, P. Y. Ge, H. Vrubel, X. Hu, H. H. Girault, *Energy Environ. Sci.* **2011**, *4*, 4246–4251.
- [7] P. Ge, T. K. Todorova, I. H. Patir, A. J. Olaya, H. Vrubel, M. Mendez, X. Hu, C. Corminboeuf, H. H. Girault, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 11558–11563.
- [8] P. Ge, A. J. Olaya, M. D. Scanlon, I. Hatay Patir, H. Vrubel, H. H. Girault, *ChemPhysChem* **2013**, *14*, 2308–2316.
- [9] L. Rivier, T. J. Stockmann, M. A. Méndez, M. D. Scanlon, P. Peljo, M. Opallo, H. H. Girault, *J. Phys. Chem. C* **2015**, *119*, 25761–25769.
- [10] P. Peljo, M. D. Scanlon, A. J. Olaya, L. Rivier, E. Smirnov, H. H. Girault, *J. Phys. Chem. Lett.* **2017**, *8*, 3564–3575.
- [11] L. Rivier, P. Peljo, L. A. C. Vannay, G. C. Gschwend, M. A. Méndez, C. Corminboeuf, M. D. Scanlon, H. H. Girault, *Angew. Chemie - Int. Ed.* **2017**, *56*, 2324–2327.
- [12] L. Rivier, P. Peljo, S. Maye, M. A. Méndez, H. Vrubel, L. A. C. Vannay, C. Corminboeuf, M. D. Scanlon, H. H. Girault, *Chem. - A Eur. J.* **2019**, *25*, 12769–12779.
- [13] J. Jedraszko, W. Adamiak, W. Nogala, H. H. Girault, M. Opallo, *J. Electroanal. Chem.* **2018**, *819*, 101–106.
- [14] A. F. Molina-Osorio, A. Gamero-Quijano, P. Peljo, M. D. Scanlon, *Curr. Opin. Electrochem.* **2020**, *21*, 100–108.
- [15] H. H. Girault, in *Dev. Electrochem. Sci. Inspired by Martin Fleischmann* (Eds.: D. Pletcher, Z.-Q. Tian, D.E. Williams), John Wiley & Sons, Ltd., **2014**, pp. 295–308.
- [16] S. Rastgar, M. Pilarski, G. Wittstock, *Chem. Commun.* **2016**, *52*, 11382–11385.
- [17] S. Rastgar, G. Wittstock, *J. Phys. Chem. C* **2017**, *121*, 25941–25948.
- [18] S. Rastgar, G. Wittstock, *J. Phys. Chem. C* **2018**, *122*, 12963–12969.
- [19] M. D. Scanlon, P. Peljo, L. Rivier, H. Vrubel, H. H. Girault, *Phys. Chem. Chem. Phys.* **2017**, *19*, 22700–22710.

- [20] V. J. Cunnane, G. Beblewicz, D. J. Schiffrin, *Electrochim. Acta* **1995**, *40*, 3005–3014.
- [21] M. D. Scanlon, X. Bian, H. Vrubel, V. Amstutz, K. Schenk, X. Hu, B. Liu, H. H. Girault, *Phys. Chem. Chem. Phys.* **2013**, *15*, 2847.
- [22] X. Bian, M. D. Scanlon, S. Wang, L. Liao, Y. Tang, B. Liu, H. H. Girault, *Chem. Sci.* **2013**, *4*, 3432–3441.
- [23] P. Ge, M. D. Scanlon, P. Peljo, X. Bian, H. Vubrel, A. O’neill, J. N. Coleman, M. Cantoni, X. Hu, K. Kontturi, B. H. Liu, H. H. Girault, *Chem. Commun.* **2012**, *48*, 6484–6486.
- [24] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253–278.
- [25] J. Li, N. Wu, *Catal. Sci. Technol.* **2015**, *5*, 1360–1384.

Table of contents graphic



Closing the loop. Consuming a sacrificial electron donor to generate H_2 as a solar fuel is not a sustainable clean energy strategy. The oxidised donor must be regenerated in a renewable manner. A novel approach is outlined to close the loop and photo-regenerate the sacrificial electron donor decamethylferrocene (DcMFC) in a biphasic H_2 evolution scheme using core-shell semiconductor nanoparticles and phase-transfer of the oxidised donor ($DcMFC^+$).

Institute and/or researcher Twitter usernames: @M_D_Scanlon; @GiraultHubert