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ARTICLE

## Light Driven Styrene Epoxidation and Hydrogen Generation Using H<sub>2</sub>O as an Oxygen Source in a Photoelectrosynthesis Cell

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

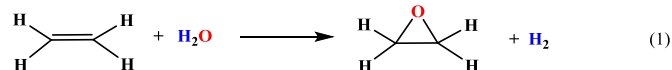
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A dye-sensitized photoelectrosynthesis cell (DSPEC) has been prepared for the oxidation of alkenes to epoxides and evolution of hydrogen using water as an oxygen source and sunlight. A Ru oxidation catalyst, **2,2**<sup>†</sup>, is used in homogeneous phase in the anodic compartment to oxidize a water-soluble alkene, 4-styrene sulfonic acid (4-HSS), to the corresponding epoxide that in acidic solution is hydrolyzed to the diol (4-(1,2-dihydroxyethyl)-benzenesulfonic acid). Concomitantly, protons are generated that diffuse through a proton exchange membrane to a Pt cathode where they are transformed into hydrogen. Illumination under 1.5 AMG (100 mW cm<sup>-2</sup>) together with an external bias of 0.3 V vs. NHE after 24 h, leads to the generation of 1.28 Coulombs together with the formation of 6.1 μmol of H<sub>2</sub> at the cathodic compartment that corresponds to a faradaic efficiency of 92%. In addition 0.7 mM of the 4-HSS substrate has been oxidized at the anodic compartment with a conversion yield of 7%. The rate of hydrogen evolution is limited by the oxidation of the organic substrate, and the TOF for both reactions is measured to be 0.8 ks<sup>-1</sup>.

### INTRODUCTION

Epoxides are highly useful intermediates for the production of a variety of important commercial products,<sup>1,2</sup> and therefore their synthesis is a subject of substantial academic and industrial interest. Olefin epoxidation is one of the main paths that lead to the production of epoxides both at a laboratory and at the industrial scale.<sup>3</sup> While molecular oxygen can be used for the epoxidation of ethylene, the majority of alkene epoxidation reactions are carried out using stoichiometric amounts of alkylhydroperoxides or peracids, with the formation of the corresponding alcohol or carboxylic acid respectively as an undesired side product. In addition, from a safety perspective, peracids are relatively hazardous chemicals. In this respect, there is a strong need for the development of new epoxidation methods that make use of safer oxidants and minimize waste products. The employment of hydrogen peroxide is an attractive option both on environmental and economic grounds<sup>4-7</sup> giving just water as a byproduct. Another option is to use water as the source of oxygen for the epoxidation reaction with the formation of hydrogen as a valuable side product as indicated in the



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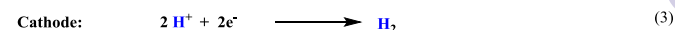
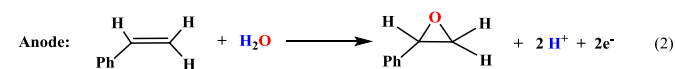
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<sup>†</sup> Electronic Supplementary Information (ESI) available: Experimental section containing the preparation of photoanodes and modified membranes, cell construction and additional spectroscopic, electrochemical, and catalytic data. See DOI: 10.1039/x0xx00000x

equation below,<sup>8</sup> which involves the input of 37.35 Kcal mol<sup>-1</sup> given its uphill thermodynamics that can be provided thermally<sup>9,10</sup> or photochemically<sup>11</sup> with sunlight. This strategy also benefits from the formation of hydrogen as a byproduct that is also a clean energy vector.<sup>12,13</sup> Given the fact that the worldwide production of ethylene oxide represents 20 million tons per year,<sup>14</sup> and assuming that the reaction is driven by sunlight and with a 100 % atom economy, it would represent around 0.9 million tons of hydrogen produced in that process, or 2500 tons of hydrogen per day. In terms of energy, this represents the production of an impressive 2700 MWh per day just for this reaction. The same conceptual scheme can be applied for the oxidation of aldehydes to acids, the oxidation of organic sulfides to sulfoxides, etc.

To achieve the reaction shown in equation (1), a set of reactions catalyzed by transition metal complexes is needed. For the thermal case,<sup>9</sup> Ru pincer type of complexes have been used for the oxidation of aldehydes to carboxylic acids and formation of hydrogen with a single catalyst in homogeneous phase.

A different strategy consists on taking advantage of the intrinsic redox nature of the chemical reactions occurring and separating the single reaction shown in equation (1) into two half reactions. This would allow building an electrochemical cell where the oxidation of the alkene will take place at the anode and the proton reduction will occur at the cathode, as depicted for styrene in equations (2) and (3) respectively.



Furthermore, if the reaction is to be driven photochemically, a light harvesting molecule is needed since sunlight interacts with H<sub>2</sub>O and alkenes mainly at a vibrational level. Thus a series of additional reactions involving light harvesting molecules capable of interacting with suitable catalysts will need to be designed in order to break and form the desired bonds at a reasonable rate.

The oxidation of substrates induced by visible light using water as an oxygen source has been previously described in the literature in homogeneous phase using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy is 2,2'-bipyridine) as a light harvesting molecule coupled to a sacrificial electron acceptor (SEA), such as sodium persulfate or Co(III) complexes like [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>.<sup>15-19</sup> Other examples include the use of catalyst-photosensitizer dyad systems that can oxidize alcohols, sulfides and alkenes.<sup>20-25</sup> On the other hand the reduction of protons has also been achieved with a variety of sacrificial electron donors (SED).<sup>26,27</sup> In both cases the sacrificial agents react fast and in an irreversible manner so that they favor only the desired reactions. The development of photoelectrosynthesis cells (DSPEC) to carry out the reaction in equation (1) implies necessarily the absence of sacrificial agents and thus introduces further difficulties in its overall implementation.<sup>28-37</sup> Today there is an urgent need to build DSPECs and understand and master all the kinetic and thermodynamic parameters involved in such a cell so that efficient devices can be obtained.

With all this in mind, we have designed a DSPEC using FTO/TiO<sub>2</sub>-P-bpy-Ru (where FTO is fluorine doped tin oxide, P-bpy-Ru is [Ru<sup>II</sup>(P-bpy)(bpy)<sub>2</sub>]<sup>2+</sup>, P-bpy is 2,2'-bipyridine-4,4'-bis(phosphonic acid), bpy is 2,2'-bipyridine) as a photoanode and a Pt mesh as a cathode. The oxidation catalyst will be present in homogeneous phase since this configuration gives a high degree of flexibility with regard to the selection and use of potential catalysts and reactions. The latter has to comply with two indispensable requirements: a) the catalyst has to act efficiently with regard to substrate oxidation and b) the active site of the catalyst needs to be regenerated very fast by the photoanode. Finally, a specific proton exchange membrane based on a combination of Nafion® and poly(3,4-ethylenedioxythiophene) (PEDOT) has been designed so that cationic species in the anodic compartment do not block the proton channel.

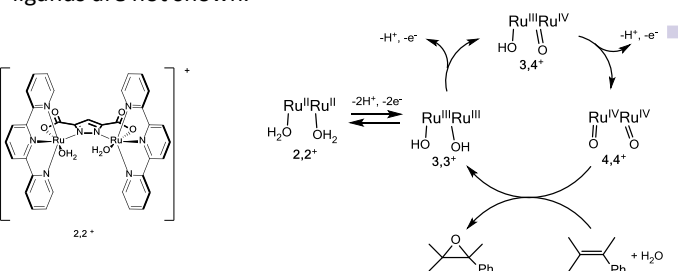
Here on we report a two compartment DSPEC cell for H<sub>2</sub> generation and epoxidation of alkenes using visible light and water and its complete kinetic and thermodynamic characterization.

## RESULTS AND DISCUSSION

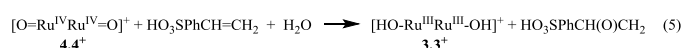
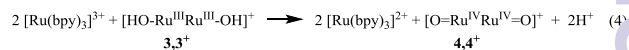
### 2.1 Alkene epoxidation catalyzed by 2,2<sup>+</sup> in homogeneous phase.

We have recently reported a dinuclear Ru-aqua 2,2<sup>+</sup> complex, whose structure is shown in Figure 1 and that contains a dinucleating trianionic ligand backbone (pyrazolate-3,5-dicarboxylate, pdc<sup>3-</sup>) that bridges the two Ru metal centers and a tridentate meridional ligand (2,2':6',2''-terpyridine, trpy) that

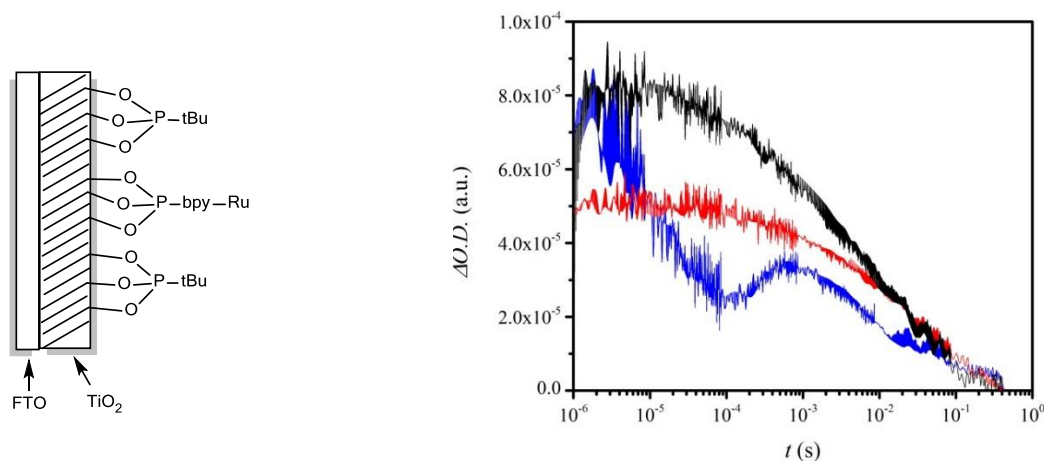
completes the octahedral geometry around the metal center. Complex 2,2<sup>+</sup> has been shown to be a powerful epoxidation catalyst for a variety of alkenes including styrene (TOF<sub>i</sub> > 2.9 s<sup>-1</sup>)<sup>38</sup> in organic solvents and using PhIO as sacrificial oxidant. The catalytic mechanism proposed is shown in Figure 1. In order to introduce the 2,2<sup>+</sup> catalyst into a DSPEC cell it is indispensable that it also works in water and is activated by 1e<sup>-</sup> outer sphere electron transfer oxidants such as [Ru(bpy)<sub>3</sub>]<sup>3+</sup>. For this purpose we have carried out the photochemically induced generation of [Ru(bpy)<sub>3</sub>]<sup>3+</sup> in water using [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> (Co<sup>III</sup>) as a sacrificial electron acceptor in the presence of the water soluble sodium 4-styrene sulfonate as substrate. Since we have carried out all the reactions at pH = 1.0, the latter is protonated forming 4-styrene sulfonic acid (4-HSS).<sup>39</sup>



A deoxygenated solution containing 2,2<sup>+</sup> 0.01 mM/4-HSS 10 mM/[Ru(bpy)<sub>3</sub>]<sup>2+</sup> 0.1 mM/Co<sup>III</sup> 10 mM in 4 mL of a D<sub>2</sub>O:CF<sub>3</sub>SO<sub>3</sub>D mixture (pD 1.0) was irradiated with visible light for 30 min and generated 1.1 mM 4-(1,2-dihydroxyethyl)-benzenesulfonic acid. The latter is a known phenomenon due to the ring-opening hydrolysis of the epoxide under acidic conditions, and was already reported by Fukuzumi *et al.* for the chemical oxidation of epoxides using a Ru catalyst.<sup>40</sup> The conversion of the initial substrate reached 30% that represents a TOF of 0.17 s<sup>-1</sup> (see Figure S1 for details). This results shows that [Ru(bpy)<sub>3</sub>]<sup>3+</sup> is capable of activating the catalyst to its active state, 4,4<sup>+</sup> (see Figure 1 and equation (4)), and that the latter is capable of oxidizing the styrene substrate to styrene



**Figure 2.** Left, schematic drawing of a photoanode. Right, transient absorption spectroscopy (TAS) kinetics of **FTO/TiO<sub>2</sub>-P-bpy-Ru, TiO<sub>2</sub>-P-tBu/** photoanodes in a 0.1 M LiClO<sub>4</sub>/HClO<sub>4</sub> aqueous solution (pH 1.0) in the presence of 42.5 mM 4-HSS. Black, in the absence of catalyst; red, with the addition of 30 μM **3,3<sup>+</sup>**; blue, with the addition of 220 μM **3,3<sup>+</sup>**. TAS kinetics were recorded under 10 mW cm<sup>-2</sup>, using laser excitation pulses at 450 nm and recorded at 650 nm.



oxide that is finally hydrolyzed to the corresponding diol (equations 4-6). The reaction mechanism for this catalyst was previously studied in our group.<sup>38</sup> If no **4,4<sup>+</sup>** had been produced, only the oxidation by [Ru(bpy)<sub>3</sub>]<sup>3+</sup> would have been observed. In that case, the reaction without catalyst is not selective and produced only the aldehyde derivative (see Figure S1).

## 2.2 The performance of the photoanode

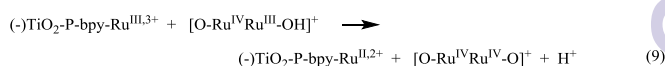
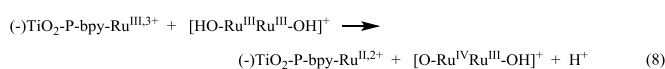
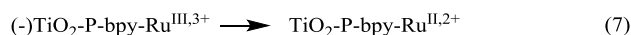
As a photoanode we use FTO coated with TiO<sub>2</sub> containing both P-bpy-Ru<sup>II,2+</sup> and *tert*-butylphosphonic acid (P-tBu), (see Figure S3 for UV-vis spectroscopic characterization). The latter minimizes interactions of the catalyst with the TiO<sub>2</sub> surface and thus avoids undesirable back electron transfer (ET) reactions improving the yield of the productive reactions. The same strategy has been used in dye sensitized solar cells (DSC) with phosphinate amphiphiles.<sup>41,42</sup> We label this photoanode as **FTO/TiO<sub>2</sub>-P-bpy-Ru, TiO<sub>2</sub>-P-tBu/** and a schematic drawing of its structure is offered in Figure 2. Transient absorption spectroscopy (TAS) was carried out in 0.1 M LiClO<sub>4</sub>/HClO<sub>4</sub> aqueous solution at pH = 1.0 with this photoanode in the presence of the catalyst and substrate in order to check the capacity of this anode to activate the catalyst with light and to kinetically characterize the reactions involved.

Figure 2 shows the results obtained upon illuminating under 10 mW cm<sup>-2</sup>, using laser excitation pulses at 450 nm and recording at 650 nm where the anchored [Ru(bpy)<sub>3</sub>]<sup>3+</sup> moiety

has a broad absorption band. In black is shown the kinetics in the absence of catalyst whereas the red trace contains 30 μM **3,3<sup>+</sup>** and the blue one 220 μM **3,3<sup>+</sup>**. We add the catalyst in oxidation state 3,3 since, as we have shown previously,<sup>38</sup> the lower oxidation states are precursor to the real catalytic species that are in oxidation states **3,4<sup>+</sup>** and **4,4<sup>+</sup>** as indicated at the right hand side of Figure 1.

In Figure 3 is depicted a scheme that summarizes the most significant reactions that can occur at the photoanode compartment and that will be analyzed in detail here on. In the absence of catalyst the system decays with a half lifetime of about 4.1 ms which is attributed to the recombination reaction shown in eq. 7 (red arrow 6 in Figure 3) once the electron is injected into the TiO<sub>2</sub> conduction band. The latter is known to happen within the picosecond time scale.<sup>43</sup>

In the presence of low concentration of catalyst **3,3<sup>+</sup>** the **bpy-Ru<sup>III,3+</sup>** signal decays at a similar rate. However as the catalyst concentration is increased from 30 to 220 μM the decay of the **bpy-Ru<sup>III,3+</sup>** signal becomes faster by almost an order of magnitude with a  $t_{1/2} \approx 0.02$  ms. A dependence of dye





external bias. Both photocurrent intensities and hydrogen evolution are monitored and are depicted in Figure 4 (down). After 24 h, 1.28 C (13.2  $\mu\text{mol}$  of electrons) have passed through the external circuit together with the formation of 6.1  $\mu\text{mol}$  of  $\text{H}_2$  at the cathodic compartment that corresponds to a faradaic efficiency of 92%. In addition 0.5 mM of the 4-HSS substrate have been oxidized to 4-(1,2-dihydroxyethyl)-benzenesulfonic acid (see Figure S7) at the anodic compartment. Overall, a 7% conversion yield was found from the disappearance of the starting material, corresponding to 70% selectivity towards diol formation, which is in accordance with the selectivity of catalyst **2,2<sup>+</sup>** in chemical oxidation reactions.<sup>38</sup> This represents 70 TON with a TOF of 0.8  $\text{ks}^{-1}$  for the oxidation of the organic substrate and 68 TON with a TOF of 0.8  $\text{ks}^{-1}$  for the production of hydrogen. In the absence of the organic substrate or Ru-catalyst or Ru-photosensitizer, the currents obtained were negligible in all cases (see Figure S6). As can be observed in Figure 4 (down), as the photocatalytic reaction proceeds the current intensity decreases up to practically zero after 24 h. The main deactivation pathway is de-attachment of the Ru-phosphonate dye from the surface of the  $\text{TiO}_2$  due to the hydration of the phosphonate bipyridyl ligands (see Figure S8). It can thus be inferred that the current intensity decrease over time shown in Figure 4 (down) basically correlates with Ru leaching. This low stability of the dye on the  $\text{TiO}_2$ -surface is a phenomenon that has been reported earlier<sup>51</sup> and that needs to be dramatically minimized in order to build more stable devices. Promising solutions involve the use of atomic layer deposition (ALD),<sup>52</sup> electropolymerization of alkene functionalized dyes<sup>53</sup> or dip-coating of polymers,<sup>54</sup> all of which have proven to improve the stability of photosensitizers in DSPEC.

This model DSPEC represents the first example of a molecular device that performs the epoxidation of an alkene and production of hydrogen simultaneously using the most abundant and green reagents available: sunlight and water. It is also the first example where the catalysts operates in homogeneous phase and thus gives a large flexibility to the system since the catalyst can be easily changed. The configuration used here in turn also allows foreseeing a large scope, of not only different type of catalytic oxidative reactions but also of substrates to be converted.

The literature related to using water as oxygen source and at the same time generate dihydrogen, is extremely scarce and limited solely to the oxidation of alcohols.<sup>9,36,55</sup> An interesting example is described for the oxidation of benzylalcohol to benzaldehyde and hydrogen generation but with much lower operation times and much lesser faradaic efficiencies.<sup>36</sup>

## Conclusions

The use of water as an oxygen source in combination with sunlight for the oxidation of organic substrates is one of the hot topics the green oxidation chemistry is facing today. In the present paper we present for the first time a model DSPEC that transform alkenes into the corresponding diols via

epoxidation catalysis with simulated sunlight and small potential applied bias. In addition the byproduct is hydrogen that can be used as a solar fuel. Here we establish the thermodynamics and kinetics of the main reactions involved in the cell. We also underline the unproductive reactions as well as the decomposition pathways that need to be improved to come up with a technologically useful device. It is also important to highlight that the present model DSPEC configuration possesses a high degree of chemical versatility since the catalyst is used in homogeneous phase and thus it can be adapted to other substrates provided the right catalyst is used.

## Acknowledgements

We thank MINECO (CTQ-2013-49075-R, SEV-2013-0319-CTQ2014-52974-REDC), the EU COST actions CM1202 and CM1205, and "LaCaixa Foundation". PG-B thanks "LaCaixa Foundation" for a PhD grant. CDG is grateful for an FPI grant from MINECO. EP and JC would like to thank ICIQ and ICREA for their financial support.

## References

- G. Grigoropoulou, J. H. Clark and J. A. Elings, *Green Chem.*, 2003, **5**, 1-7.
- K. Bauer, D. Garbe and H. Surburg, In *Common Fragrance and Flavor Materials*; Wiley-VCH: New York/Weinheim; 1997.
- G. Siel, R. Rieth and K. T. Rowbottom, In *Ullmann's Encyclopedia of Organic Chemicals*; Wiley-VCH: Weinheim; 1999.
- K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J. Org. Chem.*, 1996, **61**, 8310.
- K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 905.
- R. R. L. Martins, M. G. P. M. S. Neves, A. J. D. Silvestre, M. M. Q. Simões, A. M. S. Silva, A. C. Tomé, J. A. A. Cavaleiro, P. Tagliatesta and C. Crestini, *J. Mol. Catal.*, 2001, **172**, 33.
- R. I. Kureshy, N. H. Khan, S. H. R. Abdi, S. T. Patel and R. V. Jasra, *Tetrahedron-Asymmetry*, 2001, **12**, 433.
- R. H. Holm and J. P. Donahue, *Polyhedron*, 1993, **12**, 571.
- E. Balaraman, E. Khaskin, G. Leitus and D. Milstein, *Nat. Chem.*, 2013, **5**, 122-125.
- J. H. Choi, L. E. Heim, M. Ahrens and M. H. Prechtel, *Dalton Trans.*, 2014, **43**, 17248-17254.
- P. Farràs, C. Di Giovanni, J. N. Clifford, E. Palomares and A. Llobet, *Coord. Chem. Rev.*, 2015, **304**, 202-208.
- D. Kalita, B. Radaram, B. Brooks, P. P. Kannam and X. Zhao, *ChemCatChem*, 2011, **3**, 571-573.
- L. Zang, In *Energy Efficiency and Renewable Energy Through Nanotechnology*; Springer: Berlin, 2011.
- "Ethylene Oxide". *WP Report*. SRI Consulting. January 2009. Retrieved 2009-09-29.
- S. Fukuzumi, T. Kishi, H. Kotani, Y. M. Lee and W. Nam, *Nat. Chem.*, 2011, **3**, 38-41.
- F. Li, M. Yu, Y. Jiang, F. Huang, Y. Li, B. Zhang and L. Sun, *Chem. Commun.*, 2011, **47**, 8949-8951.
- S. Ohzu, T. Ishizuka, Y. Hirai, S. Fukuzumi and T. Kojima, *Chem. Eur. J.*, 2013, **19**, 1563-1567.
- X. Zhou, F. Li, X. Li, H. Li, Y. Wang and L. Sun, *Dalton Trans.* 2014, **44**, 475-479.

- 19 P. Farràs and A. C. Benniston, *Tetrahedron Lett.*, 2014, **55**, 7011.
- 20 W. Chen, F. Rein and R. Rocha, *Angew. Chem. Int. Ed.*, 2009, **121**, 9852-9855.
- 21 W. Chen, F. Rein, B. Scott and R. Rocha, *Chem. Eur. J.*, 2011, **17**, 5595-5604.
- 22 M. Hajimohammadi, N. Safari, H. Mofakham and F. Deyhimi, *Green Chem.*, 2011, **13**, 991-997.
- 23 O. Hamelin, P. Guillo, F. Loiseau, M. Boissonnet and S. Menage, *Inorg. Chem.*, 2011, **50**, 7952-7954.
- 24 P. Farràs, S. Maji, J. Benet-Buchholz and A. Llobet, *Chem. Eur. J.*, 2013, **19**, 7162-7172.
- 25 T. T. Li, F. M. Li, W. L. Zhao, Y. H. Tian, Y. Chen, R. Cai and W. F. Fu, *Inorg. Chem.*, 2015, **54**, 183-191.
- 26 Z. Han and R. Eisenberg, *Accounts Chem. Res.*, 2014, **47**, 2537-2544.
- 27 S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll and A. Llobet, *Chem. Soc. Rev.*, 2014, **43**, 7501-7519.
- 28 W. Youngblood, S. Lee, Y. Kobayashi, E. Hernandez-Pagan, P. Hoertz, T. Moore, A. Moore, D. Gust and T. Mallouk, *J. Am. Chem. Soc.*, 2009, **131**, 926-927.
- 29 R. Brimblecombe, A. Koo, G. Dismukes, G. Swiegers and L. Spiccia, *J. Am. Chem. Soc.*, 2010, **132**, 2892-289.
- 30 L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2010, **46**, 7307.
- 31 G. F. Moore, J. D. Blakemore, R. L. Milot, J. F. Hull, H. E. Song, L. Cai, C. A. Schmuttenmaer, R. H. Crabtree and G. W. Brudvig, *Energy Environ. Sci.*, 2011, **4**, 2389.
- 32 Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li and L. Sun, *J. Am. Chem. Soc.*, 2013, **135**, 4219-4222.
- 33 L. Alibabaei, M. K. Brennaman, M. R. Norris, B. Kalanyan, W. Song, M. D. Losego, J. J. Concepcion, R. A. Binstead, G. N. Parsons and T. J. Meyer, *Proc. Natl. Acad. Sci. U.S.A.*, 2013, **110**, 20008.
- 34 Y. Gao, L. Zhang, X. Ding and L. Sun, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12008.
- 35 X. Ding, Y. Gao, L. Zhang, Z. Yu, J. Liu and L. Sun, *ACS Catal.*, 2014, **4**, 2347.
- 36 W. Song, A. K. Vannucci, B. H. Farnum, A. M. Lapidès, M. K. Brennaman, B. Kalanyan, L. Alibabaei, J. J. Concepcion, M. D. Losego, G. N. Parsons and T. J. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 9773.
- 37 Z. Yu, F. Li and L. Sun, *Energ. Environ. Sci.*, 2015, **8**, 760-775.
- 38 C. Di Giovanni, A. Poater, J. Benet-Buchholz, L. Cavallo, M. Solà and A. Llobet, *Chem. Eur. J.*, 2014, **20**, 3898.
- 39 L. Li, L. Feng, Y. Wei, C. Yang and H. F. Ji, *J. Colloid Interface Sci.*, 2012, **381**, 11-16.
- 40 Y. Hirai, T. Kojima, Y. Mizutani, Y. Shiota, K. Yoshizawa and S. Fukuzumi, *Angew. Chem. Int. Ed.*, 2008, **47**, 5772-5776.
- 41 M. Wang, X. Li, H. Lin, P. Pechy, S. M. Zakeeruddin and M. Grätzel, *Dalton Trans.*, 2009, **45**, 10015-10020.
- 42 D. V. Pogozhev, M. J. Bezdek, P. A. Schauer and C. P. Berlinguette, *Inorg. Chem.*, 2013, **52**, 3001-3006.
- 43 F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant and E. Reisner, *Chem. Eur. J.*, 2012, **18**, 15464-15475.
- 44 I. Montanari, J. Nelson and J. R. Durrant, *J. Phys. Chem. B*, 2002, **106**, 12203-12210.
- 45 J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Grätzel and J. R. Durrant, *J. Phys. Chem. C*, 2007, **111**, 6561-6567.
- 46 Z. Qi, In *Proton Exchange Membrane Fuel Cells*; CRC Press, 2013.
- 47 L. Li, J. Drillet, R. Dittmeyer and K. Jüttner, *J. Solid State Electrochem.*, 2006, **10**, 708-713.
- 48 M. K. Brennaman, A. P. T. Patrocínio, W. Song, J. W. Jurss, J. J. Concepcion, P. G. Hoertz, M. C. Traub, N. Y. Murakami Iha and T. J. Meyer, *ChemSusChem*, 2011, **4**, 216-227.
- 49 J. E. Benedetti, M. A. de Paoli and A. F. Nogueira, *Chem. Commun.*, 2008, **9**, 1121-1123.
- 50 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.
- 51 K. Hanson, M. K. Brennaman, H. Luo, C. R. Glasson, J. J. Concepcion, W. Song and T. J. Meyer, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1462-1469.
- 52 K. Hanson, M. D. Losego, B. Kalanyan, D. L. Ashford, G. N. Parsons and T. J. Meyer, *Chem. Mater.*, 2013, **25**, 3-5.
- 53 A. M. Lapidès, D. L. Ashford, K. Hanson, D. A. Torelli, J. L. Templeton and T. J. Meyer, *J. Am. Chem. Soc.*, 2013, **135**, 15450-15458.
- 54 K.-R. Wee, M. K. Brennaman, L. Alibabaei, B. H. Farnum, B. Sherman, A. M. Lapidès and T. J. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 13514-13517.
- 55 T. P. A. Ruberu, N. C. Nelson, I. I. Slowing, J. Vela, *J. Phy. Chem. Lett.*, 2012, **3**, 2798-2802.