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DOI

[10.1002/chem.202003306](https://doi.org/10.1002/chem.202003306)

Publication date

2021

Document Version

Final published version

Published in

Chemistry-A European Journal

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[Link to publication](#)

Citation for published version (APA):

Bruggeman, D. F., Bakker, T. M. A., Mathew, S., & Reek, J. N. H. (2021). Redox-Mediated Alcohol Oxidation Coupled to Hydrogen Gas Formation in a Dye-Sensitized Photosynthesis Cell. *Chemistry-A European Journal*, 27(1), 218-221. <https://doi.org/10.1002/chem.202003306>

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Photocatalysis

Redox-Mediated Alcohol Oxidation Coupled to Hydrogen Gas Formation in a Dye-Sensitized Photosynthesis Cell

Didjay F. Bruggeman, Tijmen M. A. Bakker, Simon Mathew, and Joost N. H. Reek^{*[a]}

Abstract: This work reports a dye-sensitized photoelectrochemical cell (DSPEC) that couples redox-mediated light-driven oxidative organic transformations to reductive hydrogen (H₂) formation. The DSPEC photoanode consists of a mesoporous anatase TiO₂ film on FTO (fluorine-doped tin oxide), sensitized with the thienopyrroledione-based dye AP11, while H₂ was formed at a FTO-Pt cathode. Irradiation of the dye-sensitized photoanode transforms 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) to the oxidized TEMPO (TEMPO⁺), which acts as a chemical oxidant for the conversion of benzyl alcohol. The TEMPO^{0/+} couple, previously used as redox mediator in DSSC, mediates efficient electron transfer from the organic substrate to the photo-oxidized dye. A DSPEC photoreactor was designed that allows *in situ* monitoring the reaction progress by infrared spectroscopy and gas chromatography. Sustained light-driven oxidation of benzyl alcohol to benzaldehyde within the DSPEC photoreactor, using of TEMPO as mediator, demonstrated the efficiency of the device, with a photocurrent of 0.4 mA cm⁻², approaching quantitative Faradaic efficiency and exhibiting excellent device stability.

Solar energy is an attractive CO₂-neutral energy source, providing ≈4200 times the energy consumption estimated for 2035.^[1,2] Beyond widely deployed silicon-based photovoltaic (PV) technology, dye-sensitized solar cells (DSSCs)^[3] present a low-cost alternative with improved performance in low/diffuse light conditions. DSSCs use molecular dyes, wide-band gap semiconductors and redox mediators to absorb light and separate charges affording efficiencies that have surpassed 14%.^[4,5] While the application of solar-to-electric energy conversion is increasing, long-term energy storage remains a challenge. Elec-

tricity generated from PV cells can be stored indirectly into Li-ion batteries for short-term storage, or PV cells can be attached to an electrolyzer to split water and obtain H₂ as a storable fuel for long-term storage.^[6] Substitution of redox mediators in a DSSC with catalysts to furnish a dye-sensitized photoelectrochemical cell (DSPEC) to realize oxidative and reductive transformations powered by light convert light energy directly into fuels providing an alternative strategy for a solar-to-fuel device.^[7-10]

An exciting advantage for DSPECs is the opportunity to optimize the device by molecular-level design to improve light absorption, charge separation and attenuate catalytic events.^[11,12] Most examples of these devices focus on the light-driven water splitting to form O₂ and H₂,^[13] however, the solar-to-hydrogen efficiencies are still relatively low (up to 1.5%).^[14] The efficiency is partly due to the high kinetic barrier of the oxygen evolution reaction (OER),^[15] potentially leading to charge recombination. Parallel to solar fuel related chemistry lies the field of organic photoredox catalysis, a rapidly advancing topic where light is used to synthesize valuable chemicals.^[16] These fields can be elegantly combined by replacing the difficult OER to improve the performance of the DSPEC.^[17] The OER can be substituted for an alternative oxidative reaction to generate bulk chemicals with higher market values than O₂, while photogenerating a storable fuel (i.e. H₂).^[18] Initial work along these lines show that the oxidation of 5-hydroxymethylfurfural and C–H activation on BiVO₄, can be achieved in such devices.^[19,20] Recently, Meyer et al., reported the oxidation of benzyl alcohol (PhCH₂OH) to benzaldehyde (PhCHO) using a light-driven, surface-bound molecular catalyst in a DSPEC device, with reported photocurrents of 12 and 35 μA cm⁻².^[21] In this communication, we report the development of a DSPEC with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a redox mediator in solution for the light-driven oxidation of PhCH₂OH. We employed TEMPO^{0/+}-couple in solution as a redox mediator as 1) it has been successfully utilized as a redox mediator in DSSCs, indicating TEMPO⁺ production *in situ*^[22-26] and 2) having the oxidation reaction in solution instead of at the surface bound species may lead to less charge recombination and therefore higher photocurrents, 3) TEMPO⁺ is used as a sacrificial oxidant for many relevant oxidation reactions in organic synthesis so the device could be used for different reactions.^[27-31] To properly study such DSPEC we have designed a new reactor that allows *in situ* monitoring of reaction progress.

We started with initial experiments to demonstrate the viability of light-driven oxidation of PhCH₂OH in a DSPEC using

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<https://doi.org/10.1002/chem.202003306>.

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TEMPO as electron mediator to photogenerate $\text{TEMPO}^{0/+}$ as the oxidant (Figure 1). For the photooxidation of TEMPO, thienopyrroledione-based (**AP11**) was used as high-potential photosensitizer, with an oxidative power of 1.8 V upon illumination.^[32] Although DSSC based on **AP11** have not resulted in records in power conversion efficiency (PCE) it was selected because oxidation potential, providing room for future high potential redox mediators.

The initial DSPEC consisted of $\text{FTO}|\text{TiO}_2|\text{AP11}$ working electrode (WE), a fritted Pt-wire counter electrode (CE) in a glass three-electrode cell using a household lamp as illumination source (Figure S12) with the results summarized in Table 1. PhCHO generation was monitored by ATR-FT-IR (Figure S5) and photocurrent was recorded for 16 h (Figure S6). The photocurrent density (J_{SC}) of 0.1 mA cm^{-2} and PhCHO conversion are consistent with the overall light-driven oxidation proceeding with a Faradaic efficiency of 74%. A bias-free environment is desirable for industrial applications and therefore, the light-driven reaction was repeated in a two electrode system by connecting the WE directly to the CE. The system still produced PhCHO albeit with slightly lower efficiency (35%). Control experiments in absence of one of the components, (TEMPO, light or dye) afforded neglectable photocurrents (Figure S6) and also PhCHO was not produced under these conditions. These experiments demonstrate that only the full system produces photocurrent and PhCHO, indicating that the photo-oxidized dye is required to generate TEMPO^+ , which acts as

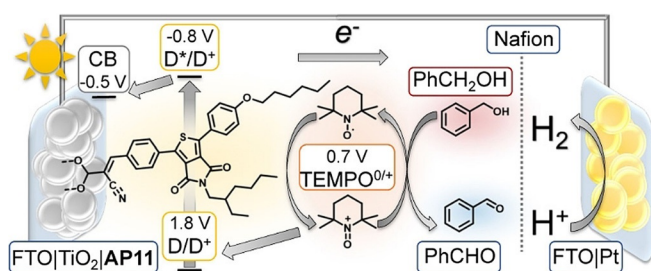


Figure 1. Schematic representation of the TEMPO mediated DSPEC system for light-driven alcohol oxidation and reductive H_2 production. D = dye, D^+ = oxidized dye, D^* = excited dye, CB = conduction band TiO_2 (anatase), with important redox potentials provided.^[32]

Table 1. Control experiments to demonstrate light-driven benzyl alcohol oxidation in a DSPEC using TEMPO as electron mediator were performed in a three-electrode cell. (WE: $\text{FTO}|\text{TiO}_2|\text{AP11}$ WE (0.79 cm^2) in 5 mL MeCN, 1.2 M LiTFSI, 1.0 M TEMPO, 0.1 M PhCH_2OH , CE: Pt-wire in 0.5 mL MeCN, 1.2 M LiTFSI and 1.0 M AcOH, separated with glass frit, 0 V vs. Ag/AgCl reference electrode (RE) and illuminated with a household LED lamp for 16 hours).

Entry	Conditions	PhCHO produced [μmol]	Electrons [$\mu\text{mol}/2$]
1	without TEMPO	0.4	1.7
2	without AP11	0	< 0
3	without cell	0	–
4	without light	0	< 0
5	without bias	13	–
6	total system	20	27.2

the *in situ* photogenerated chemical oxidant for oxidation of benzyl alcohol.

Next, we sought to optimize the photoreactor to yield maximum Faradaic efficiencies and J_{SC} . We developed a gas-tight Teflon photoreactor with WE and CE compartments featuring inlets/outlets to enable on line monitoring of the chemical conversion by ATR-FT-IR and headspace analysis by gas chromatography (GC) (Figure 2A). We assembled different sized $\text{TEMPO}^{0/+}$ -**AP11**-DSSCs to investigate possible losses in photocurrent (J_{SC}) due to the change in dimensions (surface area, and distance between the electrodes) of the system. The DSSC system applied in the photoreactor (0.64 cm^2 , Figure 2A) and in a typical sandwich DSSCs (0.19 cm^2 , Figure 2B) were measured under 1 sun (AM1.5G , 100 mW cm^{-2}) to allow literature comparison^[32,33] and with DSPEC irradiation sources: 50 mW cm^{-2} LED lamp and a household lamp (details and spectra of lamps given in Figure S12). The results and J - V curves ($N=3$ for both typical sandwich and photoreactor sized DSSC) are shown in Figure S4 and Table S1. The sandwich DSSCs measured under 1 sun revealed open-circuit voltage (V_{OC}) of 0.74 V and J_{SC} of 6.12 mA cm^{-2} . The **AP11** sandwich cells with the $\text{TEMPO}^{0/+}$ electrolyte show enhancements to the J_{SC} when compared to the reported **AP11**-DSSCs using an I^-/I_3^- electrolyte.^[32] The J_{SC} and V_{OC} are comparable to reported $\text{TEMPO}^{0/+}$ -DSSCs with different dyes, indicating efficient dye regeneration by the $\text{TEMPO}^{0/+}$ redox mediator.^[33]

To investigate the photo-performance of the system in the DSPEC set-up, the sandwich DSSC was upscaled to size of the photoreactor size (Figure 2A, 2B), and a LED lamp was used in these comparative photo-oxidation experiment (Figure 2C). Only a small reduction of 10% in J_{SC} is observed in going from the typical sandwich cell to the larger reactor, indicating only small losses due to diffusion issues. From this we established that TEMPO^+ is efficiently generated by the dye in the larger set-up, which in principle could be used for the chemical oxidation reaction.

The substrate-to-product oxidation reaction in our DSPEC reactor was independently studied by using $\text{TEMPO}(\text{BF}_4)$ ^[34] as a chemical oxidant for PhCH_2OH in order to quantify the formation of PhCHO over time. $\text{TEMPO}(\text{BF}_4)$ mimics the role of *in situ*

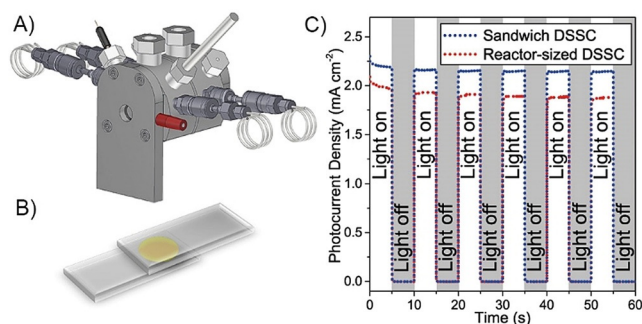


Figure 2. A) Schematic Figure of A) photo-reactor (area TiO_2 0.64 cm^2 , 6 mL) B) sandwich DSSC (area TiO_2 0.19 cm^2 , 4.71 μL) C) chopped light of sandwich (blue) and reactor size (red) DSSCs (WE: $\text{FTO}|\text{TiO}_2|\text{AP11}$, CE: $\text{FTO}|\text{Pt}$, electrolyte: 1.2 M LiTFSI, 1.0 M TEMPO, 0.1 M $\text{TEMPO}(\text{BF}_4)$ in MeCN) illuminated under 50 mW cm^{-2} LED lamp.

photogenerated TEMPO^+ in the photosynthesis cell. Therefore, PhCH_2OH (1 equiv.) was added to the electrolyte solution containing $\text{TEMPO}(\text{BF}_4)$ (2 equiv.) as the chemical oxidant. On line monitoring of chemically-driven PhCH_2OH oxidation by $\text{TEMPO}(\text{BF}_4)$ in the photoanode compartment of the DSPEC was performed over 2 h enabled by the use of by ATR-FT-IR (Figure 3A). At 16 hours $t=0$ hours, the characteristic C-O stretch (1008 cm^{-1}) from PhCH_2OH is dominant and decreased over time, with concomitant growth of the C=O stretch from PhCHO (1703 cm^{-1}) over 2 hours. Further confirmation reaction progress was through GC analysis which was fully in line with the data obtained from ATR-FT-IR.

After all individual steps of the TEMPO mediated DSPEC system in the reactor had been confirmed we performed bulk photoelectrolysis experiments in the newly designed photoreactor in order to demonstrate the simultaneous photo-generation of H_2 at the cathode and the oxidative organic transformation at the anode. The photocurrents and PhCHO production were monitored ($N=3$) over 32 hours (Figure 3B). After an induction period of 2 hours, the photocurrent showed an average of 0.4 mA cm^{-2} (Figure S10), which is a ≈ 4 -fold increase compared to our initial DSPEC experiments carried out in the three-electrode cell (Table 1). In the first 2 hours the system needs to equilibrate as benzyl alcohol oxidation leads to formation protons, which, after diffusion through the membrane to the other part of the cell, are converted to hydrogen. The proton concentration has an effect on the catalytic rates and is also known to affect the potential of the conduction band of TiO_2 as seen in water splitting DSPECs.^[35] Consistent with the preceding experiments, photocurrents and PhCHO production overlap and indicate an overall Faradaic efficiency approaching 100% when carried out in the designed photoreactor (Figure 3B, Figure S9, Table S3). Sampling of the CE compartment headspace by on line GC confirmed H_2 as the only reduction product (Figure S7), in line with a fully operative DSPEC. Most importantly, the photocurrent of 0.4 mA cm^{-2} does not degrade over the course of the experiment, demonstrating the stability of the system.

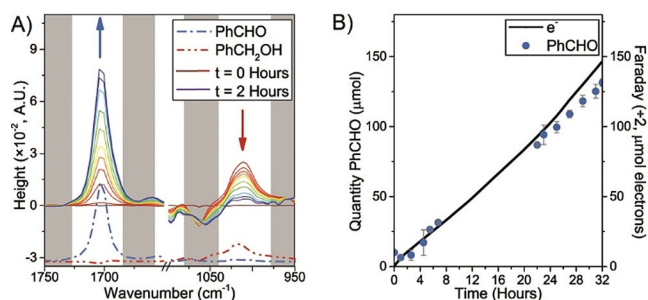


Figure 3. A) ATR-FT-IR spectra of chemical oxidation of PhCH_2OH ($t=0$ h, red) to PhCHO ($t=2$ h, violet) by $\text{TEMPO}(\text{BF}_4)$ ($t=0\text{ h} \rightarrow t=2\text{ h}$) (1.2 M LiTFSI , 0.1 M PhCH_2OH , 0.2 M $\text{TEMPO}(\text{BF}_4)$, 5 mL MeCN). B) GC quantification of light-driven PhCHO production (blue) with the anticipated amount of PhCHO based on photocurrent (black line) (WE: $\text{FTO}|\text{TiO}_2|\text{AP11}$ in 3 mL MeCN , 1.2 M LiTFSI , 1.0 M TEMPO , 0.1 M PhCH_2OH , 0.2 M $\text{C}_6\text{H}_5\text{Cl}$, CE: $\text{FTO}|\text{Pt}$ in 3 mL MeCN , 1.2 M LiTFSI , 1.0 M AcOH , 0.2 M $\text{C}_6\text{H}_5\text{Cl}$ separated by Nafion-117 proton exchange membrane, RE: 0 V vs. Ag/AgCl) illuminated with 50 mW cm^{-2} LED lamp for 32 hours.

In conclusion, we have demonstrated the light-driven chemical oxidation of organic alcohols into aldehydes, using *in situ* photogenerated TEMPO^+ from the TEMPO that is present as redox mediator in a DSPEC, and coupled to reductive H_2 production at the cathode. Photocurrent is only produced when all components are present, that is, dye, light, and TEMPO, and photooxidation occurs with a near quantitative Faradaic efficiency. Effortless on line monitoring of the formed products with ATR-FT-IR and GC is possible in our newly designed DSPEC. The DSPEC generates a photocurrent density that is ≈ 10 -fold higher than a system with a bound PhCH_2OH oxidation catalyst previously reported.^[21] We hypothesize that using TEMPO as mediator-instead of a molecular catalyst attached to the semiconductor surface-result in less charge recombination as the oxidized redox mediator can diffuse away from the surface, which will be studied in more detail in the near future.^[36] Next to the DSPEC we also report the DSSC properties of the **AP11** dye in combination with the $\text{TEMPO}^{0/+}$ redox couple which shows similar J_{SC} and V_{OC} as compared to the literature **LEG4-TEMPO** ^{$0/+$} .^[33] The J_{SC} is not as high as in record DSSC based on different dyes, however, we need the high oxidation power that is provided by the **AP11** dye. Further optimization to improve efficiency of these devices should include optimization of dyes that provide both high efficiency and high potential. Next to higher efficiencies this may also broaden the scope for photo-oxidative organic synthesis. We are currently exploring this chemistry as well as the utility of our DSPEC for upgrading biobased feedstocks to industrially relevant chemicals.

Acknowledgements

We kindly acknowledge Merck and Netherlands Organization for Scientific Research (NWO) for financial support. Dr. Eitan Oksenberg of AMOLF is gratefully thanked for the SEM measurements of the TiO_2 . Ed Zuidinga is kindly thanked for the FD-MS measurements. Remko Detz is kindly thanked for helpful discussions. Hans Ellermeijer & Daan van Giesen are kindly thanked for their contribution to the development of the cell. Tessel Bouwens is kindly thanked for useful discussions and practical advice on DSSCs.

Conflict of interest

The authors declare no conflict of interest.

Keywords: catalysis · DSPEC · hydrogen formation · light-driven hydrogen production · photo oxidation · TEMPO

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Manuscript received: July 15, 2020

Revised manuscript received: August 31, 2020

Accepted manuscript online: September 9, 2020

Version of record online: November 26, 2020