



Article scientifique

Article

2024

Published version

Public access

This is the published version of the publication, made available in accordance with the publisher's policy.

Dye-Sensitized Photocatalysis: Hydrogen Evolution and Alcohol-to-Aldehyde Oxidation without Sacrificial Electron Donor

Romito, Deborah; Maniyeri, Chinju; Nikolaou, Vasilis; Fernández-Terán, Ricardo José; Stoumpidi, Aspasia; Agapaki, Eleni; Charalambidis, Georgios; Diring, Stéphane; Vauthey, Eric; Coutsolelos, Athanassios G.; Odobel, Fabrice

How to cite

ROMITO, Deborah et al. Dye-Sensitized Photocatalysis: Hydrogen Evolution and Alcohol-to-Aldehyde Oxidation without Sacrificial Electron Donor. In: *Angewandte Chemie*, 2024, vol. 136, n° 12, p. e202318868. doi: 10.1002/ange.202318868

This publication URL: <https://archive-ouverte.unige.ch/unige:186872>

Publication DOI: [10.1002/ange.202318868](https://doi.org/10.1002/ange.202318868)

© The author(s). This work is licensed under a Creative Commons Attribution (CC BY 4.0)

<https://creativecommons.org/licenses/by/4.0>

Last deposit update in Archive ouverte UNIGE on 05.08.2025 11:55



Dye-Sensitized Photocatalysis: Hydrogen Evolution and Alcohol-to-Aldehyde Oxidation without Sacrificial Electron Donor

Deborah Romito, Chinju Govind, Vasilis Nikolaou, Ricardo J. Fernández-Terán, Aspasia Stoumpidi, Eleni Agapaki, Georgios Charalambidis, Stéphane Diring, Eric Vauthey,* Athanassios G. Coutsolelos,* and Fabrice Odobel*

Abstract: There is a growing interest in developing dye-sensitized photocatalytic systems (DSPs) to produce molecular hydrogen (H_2) as alternative energy source. To improve the sustainability of this technology, we replaced the sacrificial electron donor (SED), typically an expensive and polluting chemical, with an alcohol oxidation catalyst. This study demonstrates the first dye-sensitized system using a diketopyrrolopyrrole dye covalently linked to 2,2,6,6-tetramethyl-1-piperidine-*N*-oxyl (TEMPO) based catalyst for simultaneous H_2 evolution and alcohol-to-aldehyde transformation operating in water with visible irradiation.

Green hydrogen (H_2) is a potential clean energy carrier, stimulating the development of cheap and sustainable processes to produce this fuel from water and sunlight. In this context, artificial photosynthesis is the key process to

produce energy-rich chemical fuels from abundant feedstocks.^[1] Typical dye-sensitized photocatalytic systems (DSPs) are composed of a dye and a hydrogen evolution catalyst (HEC) co-grafted onto n-type semiconductor (n-SC) nanoparticles (NPs), such as titanium dioxide (TiO_2). These systems operate in the presence of an external sacrificial electron donor (SED) to ensure the rapid regeneration of the oxidized dye (PS^+).^[2] However, employing SEDs (typically ascorbic acid AA or triethanolamine TEOA) represents a serious obstacle for both upscaling and commercialization, since they are expensive and polluting chemicals. To improve the sustainability and applicability of DSPs, the dye regeneration could be envisaged by exploiting an oxidation reaction, which would convert abundant substrates into value-added products instead of consuming a SED. Indeed, this strategy has been thoroughly explored by coupling proton reduction with water oxidation in a photoelectrochemical cell (PEC).^[3] During this process O_2 is generally produced at the anode; however, oxygen has low economic value, and water oxidation is a kinetically and thermodynamically demanding reaction, which involves four electrons and requires high potential (1.23 V vs. Normal Hydrogen Electrode (NHE)).^[4] On the other hand, the oxidation of alcohols into their corresponding aldehydes constitutes a promising alternative, as it is significantly less kinetically challenging (involves two electrons), it has a lower redox potential (-0.14 V vs. NHE for benzyl alcohol),^[4] and it generates higher-value products.^[5] Specifically, alcohols are abundant feedstock extracted from biomass, and their corresponding carbonyl derivatives are often used as valuable synthetic precursors in both chemical and pharmaceutical industries. Using alcohol oxidation to regenerate PS^+ was recently reported with the 2,2,6,6-tetramethyl-1-piperidine-*N*-oxyl (TEMPO) catalyst in dye-sensitized photoelectrocatalytic cells (DSPECs).^[6] However, DSP is an attractive photocatalytic system owing to its simplicity in terms of preparation compared to DSPEC, which requires electrodes preparation, their wiring and a membrane to separate anolyte and catholyte. Moreover, there is only a handful of studies in DSPs employing alcohols as hole scavengers, but they are limited to methanol, ethanol and glycerol, and the efficiency and selectivity towards the carbonyl derivatives were not mentioned.^[7] Interestingly, there are recent publications from Choi and co-workers^[8] and Reisner and co-workers,^[6c] respectively, dealing with coupling photocatalytic H_2 evolu-

[*] Dr. D. Romito, Dr. V. Nikolaou, Dr. S. Diring, Dr. F. Odobel
Nantes Université, CNRS, CEISAM, UMR 6230
F-44000 Nantes (France)
E-mail: fabrice.odobel@univ-nantes.fr

Dr. C. Govind, Dr. R. J. Fernández-Terán, Dr. E. Vauthey
Department of Physical Chemistry
University of Geneva
30 Quai Ernest-Ansermet, CH-1211 Geneva (Switzerland)
E-mail: eric.vauthey@unige.ch

A. Stoumpidi, E. Agapaki, Prof. Dr. A. G. Coutsolelos
Laboratory of Bioinorganic Chemistry, Department of Chemistry
University of Crete
Voutes Campus, 70013 Heraklion, Crete (Greece)

Dr. G. Charalambidis
Theoretical and Physical Chemistry Institute

National Hellenic Research Foundation, 48 Vassileos Constantinou
Avenue, 11635 Athens (Greece)

Prof. Dr. A. G. Coutsolelos
Institute of Electronic Structure and Laser (IESL), Foundation for
Research and Technology – Hellas (FORTH), Vassilika Vouton, GR
70013 Heraklion, Crete (Greece)
E-mail: acoutsol@uoc.gr

© 2024 The Authors. Angewandte Chemie published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

tion or carbon dioxide (CO₂) reduction to selective alcohol oxidation processes, but these were only reported in PEC.

Herein, we report on an innovative DSP system for simultaneous H₂ evolution and selective benzyl alcohol oxidation working in water, without any sacrificial reagent. To accomplish this, we implemented a “photosensitizer-TEMPO” dyad (PS-TEMPO) instead of a PS, directing the regeneration of the dyad via alcohol-to-aldehyde oxidation. In addition, this photocatalytic system generates two easily separable products, namely H₂ which is released in the headspace of the reaction vessel, and aldehyde in solution which can be easily extracted (Figure 1). In this study, the dyad “PS-TEMPO” consists of a diketopyrrolopyrrole (DPP) photosensitizer covalently linked to a TEMPO catalyst (**DPP-TEMPO**, Scheme 1). DPP was selected as PS due to its high performance in dye-sensitized solar cells

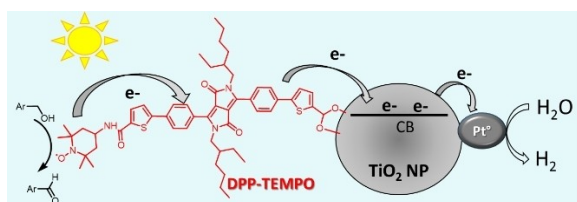


Figure 1. Schematic representation of the dual-functional photocatalytic system investigated in this work.

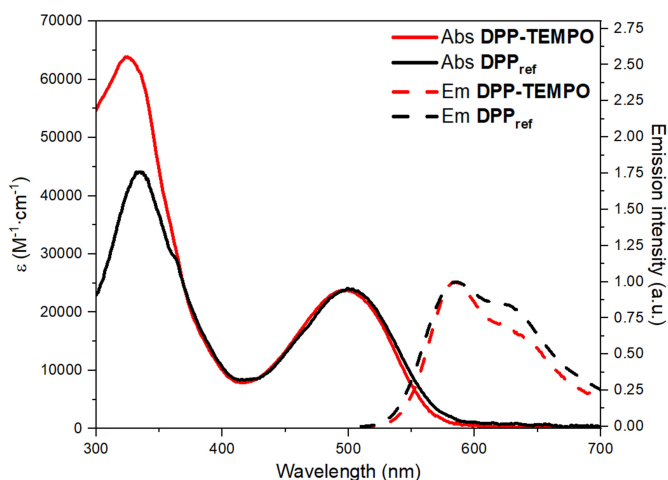


Figure 2. Absorption (solid lines) and emission (dashed lines) spectra of solutions of **DPP-TEMPO** (in red) and **DPP_{ref}** (in black) in CH₂Cl₂ at r.t. $\lambda_{excit} = 490$ nm for fluorescence spectrum.

(DSSCs)^[9] and DSPs.^[10] A DPP bearing a neopentyl amide group was also prepared (**DPP_{ref}**, Scheme 1) to explore the impact of the TEMPO moiety. Furthermore, this allowed us to compare two different DSP approaches, namely, **DPP-TEMPO** (with covalently connected PS and catalyst) versus **DPP_{ref} + TEMPO_{syn}** (co-adsorbed on TiO₂).

The synthetic route for preparing **DPP-TEMPO** and **DPP_{ref}** is illustrated in Scheme S1. All molecules were characterized by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectrometry (Figures S1–S9, see ESI for details). In the absorption spectrum of both **DPP-TEMPO** and **DPP_{ref}**, the typical $\pi-\pi^*$ transition of DPP, centered around 490 nm, can be observed (Figure 2 and Table 1). Both compounds are fluorescent but, interestingly, the emission intensity and lifetime of **DPP-TEMPO** are not reduced relative to those of **DPP_{ref}**, indicating that neither photoinduced energy nor charge transfer towards TEMPO take place to a significant extent in the dyad (Figures 2 and S19). The electrochemical properties of **DPP-TEMPO** and **DPP_{ref}** were investigated by cyclic voltammetry in CH₂Cl₂ (Table 1). The driving force of the electron injection in TiO₂ from DPP* (ΔG_{inj}), and the hole shift from oxidized DPP to TEMPO (ΔG_{reg}) indicate that all these processes are thermodynamically allowed, with $\Delta G_{inj} \approx -0.2$ eV and $\Delta G_{reg} = -0.42$ eV, respectively (Table 1).

The DSP system was then prepared by functionalizing commercially available TiO₂ NPs with Pt⁰ as HEC, and **DPP-TEMPO** as PS (see Electronic Supporting Information: ESI). Chemical binding of the dye to the TiO₂ surface via carboxylic acid was confirmed by infrared spectroscopic measurements showing the disappearance of the $\nu(C=O)$ stretching band of the free carboxylic moiety (1708 cm⁻¹) and the appearance of the new asymmetric stretching band of the O=C=O group (1638 cm⁻¹) when the dye is bound to TiO₂ (Figure S10), in agreement with a bidentate binding mode.^[12]

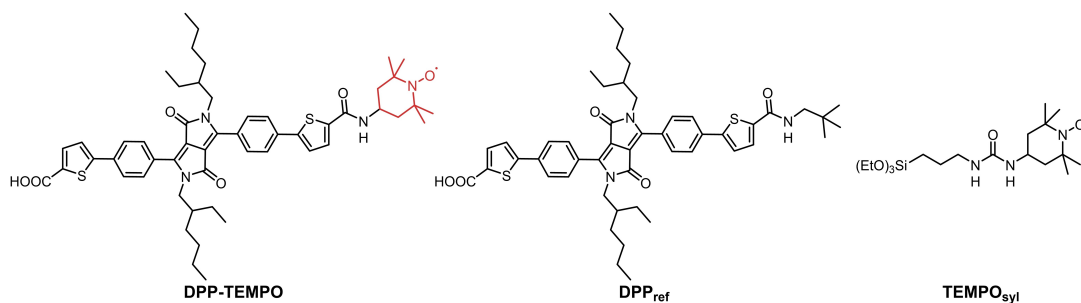
The optimal photocatalytic conditions were determined by using *p*-methoxybenzyl alcohol (MeOBenzOH) as substrate for the oxidation, as well as by screening different pH values of a borate buffer, various **DPP-TEMPO** loadings, and the effect of different concentrations of Pt⁰ on TiO₂ NPs (see ESI for details). The best catalytic performance was observed at pH = 8, with 24 nmol of **DPP-TEMPO** per mg of TiO₂ and with 3.2 nmol of Pt⁰/mg of TiO₂ (Figures 3, S11–S14, Tables 2, S1–S3). As expected, all three components of the photocatalytic system are necessary for the reaction to occur, since neither H₂ production nor aldehyde conversion

Table 1: Physico-chemical properties of **DPP_{ref}** and **DPP-TEMPO** recorded in CH₂Cl₂. All the potentials are referenced vs. saturated calomel electrode (SCE).

Dye	λ_{abs}/ϵ (nm/M ⁻¹ ·cm ⁻¹)	$\lambda_{abs}/E_{00}^{[a]}$ (nm/eV)	$E_{Ox}(\text{TEMPO}^+/\text{TEMPO})$ (V vs. SCE)	$^{[b]}E_{Ox}(\text{DPP}^+/\text{DPP})$ (V vs. SCE)	$^{[c]}\Delta G_{inj}$ (eV)	$^{[d]}\Delta G_{reg}$ (eV)
DPP_{ref}	501/2.41·10 ⁴	588/2.25	–	+1.21	–0.17	–
DPP-TEMPO	500/2.23·10 ⁴	582/2.24	+0.75	+1.17	–0.20	–0.42

^[a]Singlet excited state energy level (E_{00}) calculated with the wavelength at the intersection of normalized absorption and emission spectra;

^[b]irreversible process, here $E_{Ox} = E_a$; ^[c]calculated according to $\Delta G_{inj} = E_{Ox}(\text{DPP}^+/\text{DPP}) - E_{00} - E_{CB}(\text{TiO}_2) = -0.4 - 0.059 \cdot \text{pH}$; ^[d]calculated according to $\Delta G_{reg} = E_{Ox}(\text{TEMPO}^+/\text{TEMPO}) - E_{Ox}(\text{DPP}^+/\text{DPP})$.



Scheme 1. Molecular structures of the compounds used in this study.

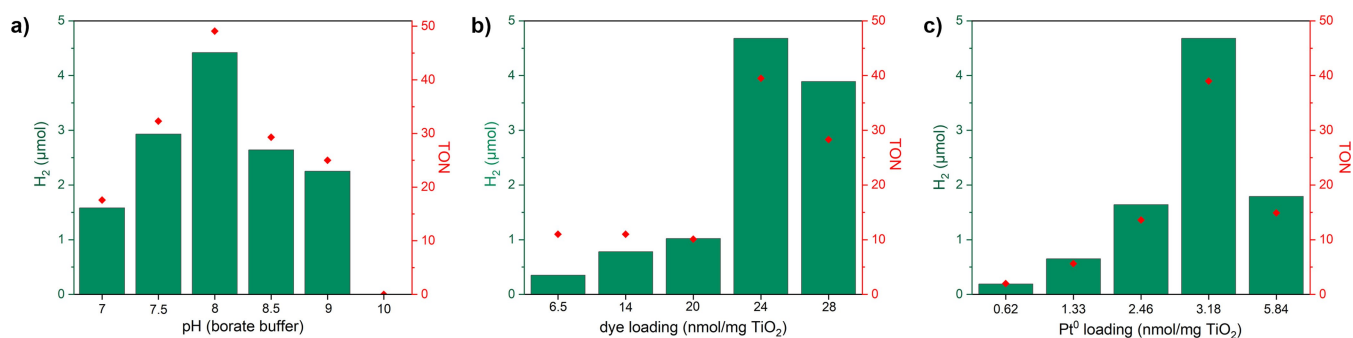


Figure 3. Photocatalytic measurements displaying H_2 production (in green) and TON (in red) obtained using **DPP-TEMPO**/ TiO_2 / Pt^0 NPs *a*) screening the buffer borate at different pH, as well as varying *b*) the dye loading and *c*) the Pt^0 coverage.

Table 2: Photocatalytic results of the DSP systems recorded under different conditions.^[a]

Entry	Dye (nmol per mg of TiO_2)/ TiO_2 / Pt^0	Alcohol	H_2		Aldehyde	
			μmol	TON	conc. (mM)	μmol
1	DPP-TEMPO (18)/ TiO_2 / Pt^0	MeOBenzOH	4.2 ± 0.2	47 ± 2	0.59 ± 0.09	2.9 ± 0.02
2	DPP-TEMPO (24)/ TiO_2 / Pt^0	MeOBenzOH	4.7 ± 0.3	39 ± 4	0.74 ± 0.09	3.7 ± 0.1
3	DPP-TEMPO (24)/ TiO_2 / Pt^0	BenzOH	2.5 ± 0.3	21 ± 2	0.27 ± 0.03	1.4 ± 0.01
4	DPP-TEMPO (24)/ TiO_2 / Pt^0	CF_3 BenzOH	3.4 ± 0.2	28 ± 2	0.42 ± 0.06	2.1 ± 0.02
5	DPP_{ref} (24)/ TiO_2 / Pt^0	MeOBenzOH	ND ^[b]	ND ^[b]	0.0025	0.012
6	TiO_2 / Pt^0	MeOBenzOH	ND ^[b]	ND ^[b]	0.0015	0.0075
7	DPP-TEMPO (24)/ TiO_2 / Pt^0	–	ND ^[b]	ND ^[b]	–	–
8	DPP_{ref} (24)/ TiO_2 / Pt^0	– ^[c]	3.5 ± 0.1	29 ± 2	–	–
9	DPP-TEMPO (18)/ TiO_2 / Pt^0	– ^[c]	8.8 ± 0.6	98 ± 8	–	–
10	DPP_{ref} (19)/ TEMPO_{syl} / TiO_2 / Pt^0	MeOBenzOH	1.0 ± 0.1	11 ± 1	0.19 ± 0.02	0.95 ± 0.01

^[a]The following standard conditions were employed: 5 mL of 0.1 M aqueous borate buffer at pH 8 + 10 mg of functionalized TiO_2 NPs/ Pt^0 (3.2 nmol); irradiation source: Green LED (525 nm, 10 mW/cm²); irradiation time: 4 hours; amount of alcohol used: 50 mM. ^[b]Not detected;

^[c]0.1 M aqueous TEOA at pH 8 was used to replace the alcohol.

are observed when one component is missing (Tables 2 and S4). Similarly, the reaction does not proceed without light irradiation, confirming that the redox reactions are actually photodriven processes. At last, the replacement of **DPP-TEMPO** by the simple **DPP_{ref}** lacking TEMPO oxidation catalyst no longer promotes H_2 evolution nor alcohol oxidation.

The larger amount of H_2 relative to the photogenerated aldehyde is intriguing. Since these two products come from a two-electron redox reaction, we could expect a 1/1 ratio. This discrepancy could be most likely due to the lower intrinsic catalytic efficiency of TEMPO compared to that of Pt^0 . Indeed, as Pt^0 is the most active HEC, it is not

unexpected that its efficiency is higher than that of TEMPO (see a more detailed discussion in ESI). Corroborating this assumption, a recent study by Reisner and co-workers also reported an unequal production of reduced and oxidized products by immobilizing a formate dehydrogenase onto TiO_2 .^[13]

As illustrated in Figure S17, H_2 evolution is interrupted after about 4 h of irradiation. To unveil the reason of the photocatalytic deactivation, **DPP-TEMPO** was desorbed from the functionalized TiO_2 NPs after photocatalysis with and without irradiation (see Figures S15–S16). The interruption of H_2 evolution is mainly attributed to: i) the photo-decomposition of the DPP photosensitizer (Figure S15)

rather than to ii) its detachment from the TiO_2 surface (Figures S12 and S16), although the instability of CO_2H anchoring group in aqueous media, and particularly in basic conditions, is well-known.^[14]

Overall, these experiments demonstrate that a DSP sensitized with **DPP-TEMPO** produces H_2 with concomitant and selective alcohol oxidation into aldehyde without any SED, reaching 50 turnover number (TON). The rate of H_2 evolution calculated during the first 3 hours of the experiment is about $200 \mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ of TiO_2 ; a value comparable to some previously published DSPs with SEDs.^[2b] Having established the optimized conditions for photocatalytic methoxy-benzyl alcohol oxidation, the scope of the substrates was expanded by testing benzyl alcohol (BenzOH) and *p*-trifluoromethyl-benzyl alcohol (CF_3BenzOH), two additional substrates with different reactivity. Interestingly, although CF_3BenzOH displays the highest oxidation potential, a larger quantity of H_2 than with BenzOH was produced (Tables 2 and S7; Figure S17). This is most likely due to the hydrophobic nature of CF_3BenzOH , which would favour a closer contact within the layer of **DPP-TEMPO** on TiO_2 NPs. Noteworthy, an analogous trend was already reported in DSPECs with a zinc porphyrin-TEMPO sensitizer.^[6c] To prove that the given photocatalytic system indeed works under sunlight, an additional photocatalytic measurement was performed using a sunlight simulator (AM 1.5 [1000 W/m^2], (Table S5). This results in a slightly lower H_2 production (3.3 μmol) and a lower TON (27), but confirms that this DSP works in real world sunlight conditions as well.

Aiming at comparing our novel approach with the classical one (using SED), photocatalytic experiments were carried out in the presence of TEOA (0.1 M, at $\text{pH}=8$) as sacrificial electron donor. Remarkably, when **DPP_{ref}** is used as sensitizer, the generated H_2 is about 30 % less compared to the respective H_2 evolution using **DPP-TEMPO** (in presence of MeOBenzOH), showing that **DPP-TEMPO** with alcohol oxidation outperforms **DPP_{ref}** with SED (Table S8, Figure S18). Secondly, it is worth noting that **DPP-TEMPO** with TEOA as SED produces twice the amount of H_2 than **DPP_{ref}** under the same conditions. This is most likely due to the longer-lived charge-separated state of **DPP-TEMPO** compared to that of **DPP_{ref}** (see transient absorption spectroscopy study below).

Previous works on DSPEC for alcohol oxidation reported that significant catalytic activities could be measured when the catalyst was simply co-grafted along with the sensitizer on the TiO_2 surface.^[6d,e] Testing the **DPP_{ref}/TEMPO_{syl}/TiO₂/Pt⁰** NPs in DSP conditions analogous to those employed with **DPP-TEMPO**, resulted in decreased photocatalytic efficiency, since both the amount of produced H_2 and aldehyde were reduced by over a factor four (~ 1 vs. $4.7 \mu\text{mol}(\text{H}_2)$, Table S9). Most likely, the weaker electronic communication between **TEMPO_{syl}** and **DPP_{ref}**, compared to that in **DPP-TEMPO**, diminishes the regeneration rate of the oxidized PS, accelerating charge recombination and degradation due to the instability of the DPP radical cation. In line with this interpretation, the exposition of the **DPP_{ref}/TEMPO_{syl}/TiO₂/Pt⁰** NPs to ambient light induces a fast bleaching within less than few hours in contrast with **DPP-**

TEMPO/TiO₂/Pt⁰ NPs, which remains colored for much longer time in the same conditions.

In another photocatalytic experiment, we have investigated the performances of a DSP in which the catalyst, in the form 4-trimethylammonium-TEMPO (10 mM), is solubilized into the borate buffer in presence of **DPP_{ref}**-functionalized TiO_2 NPs (Table S6). In these conditions, the photocatalytic performances are much lower than those achieved with the **DPP-TEMPO**, underscoring thus the advantage of the covalent dyad.

Occurrence of charge injection from **DPP-TEMPO** into TiO_2 is confirmed by transient absorption (TA) measurements, which show the formation of the DPP cation (**DPP⁺**) and an electron in the conduction band of TiO_2 in the visible (Figure 4)^[15] and mid IR (Figures S20–S21) regions.^[16] Subsequently, these features decay on several timescales ranging from a few ns to a few μs . The same measurements with **DPP_{ref}** films reveal that the decay dynamics of the **DPP⁺** band are essentially the same up to 20 ns, during which around 70 % of the initial intensity is lost (Figures S22–26). However, the remaining intensity decays with 50 ns and 1.4 μs time constants with **DPP-TEMPO** vs. 180 ns and 3.8 μs with **DPP_{ref}**. Similar differences are visible in the ground-state bleach region. These differences can be attributed to a hole shift from **DPP⁺** to the TEMPO subunit occurring on the hundred ns timescale, which results in the neutralization of **DPP⁺** and the repopulation of the electronic ground-state of the DPP subunit. The rest of the photocatalytic cycle cannot be investigated by TA since the hydroxylamine, nitroxide and oxoammonium forms of TEMPO have no spectroscopic signature in the 300–800 nm range. However, we can safely postulate that the oxoammonium can be reduced by alcohol to form the hydroxylamine and aldehyde with the release of two protons, as demonstrated in previous works.^[4,6,17] Overall, hydroxylamine is

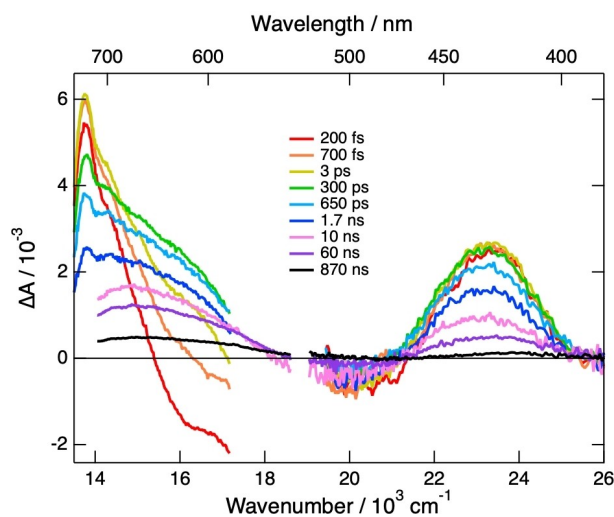


Figure 4. Transient absorption spectra recorded at various time delays after 532 nm excitation of a **DPP-TEMPO/TiO₂** film in borate buffer ($\text{pH}=8$) illustrating the decay of the locally excited state (720 and 430 nm) and build-up and decay of the DPP radical cation (680 and 430 nm), due to charge injection and recombination.

oxidized into nitroxide, and then to oxoammonium by two consecutive holes coming from DPP⁺. The holes can probably be supplied by the neighbouring PS⁺ around the dyad owing to the known lateral hole migration within dye layer on TiO₂.^[18]

In conclusion, we report for the first time on a dual-functional photocatalytic system based on TiO₂ nanoparticles sensitized by DPP-TEMPO, which simultaneously produces H₂ and oxidizes alcohols to aldehydes in water upon visible light irradiation. This is in sharp contrast to the traditional approach of DSPs, which requires SEDs for regenerating the oxidized dye; thus, rendering DSPs for H₂ evolution more compatible towards future practical applications. In addition, TEMPO can catalyze other useful oxidation reactions, i.e. preparation of imines, nitriles, and unsaturated heterocycles.^[17] Consequently, the scope of the substrates can certainly be expanded following a similar strategy. Importantly, this study gives a new impetus to DSP by showing that a two-hole oxidation process, such as alcohol oxidation, is a viable reaction to couple with a reduction reaction targeting the elimination of the SED and the generation of two added-value chemicals. Moreover, other reduction catalysts besides HECs could be implemented in the above described DSPs, such as those for CO₂ and N₂ reduction. Finally, our study shows that better performing DSPs could be engineered if a secondary electron donor is linked to the dye to prolong the final charge-separated state lifetime (e⁻/TiO₂-DPP⁺ vs. e⁻/TiO₂-TEMPO-DPP⁺). This work opens new horizons for developing DSPs without SEDs, based on the association of a dye and a TEMPO catalyst for oxidizing organic compounds. Current enhancements of the present system are ongoing in our research group and include the application of more electrochemically stable dyes than DPP, bearing stronger binding groups than the carboxylic acid.

Supporting Information

The authors have cited additional references within the Supporting Information.^[19–27]

Acknowledgements

This work received financial support under the EUR LUMOMAT project and the Investments for the Future program ANR-18-EURE-0012. This project was also supported by HORIZON TMA MSCA Postdoctoral Fellowships - European Fellowships (HORIZON-TMA-MSCA-PF-EF) action programme under the call MSCA Postdoctoral Fellowships 2021 ((HORIZON-MSCA-2021-PF-01) to V.N., grant agreement No. 101064765, SOLAR-CAT. This research was also funded by the General Secretariat for Research and Technology (GSRT) and Hellenic Foundation for Research and Innovation (HFRI; project code: 508). This research has been co-financed by the European Union and Greek national funds through the Regional Operational Program “Crete 2014–2020,” project code OPS:5029187.

Financial support from the Swiss National Science Foundation (grant nr 200020-184607) and the University of Geneva is also acknowledged. The authors greatly acknowledge AMaCC platform's team (CEISAM UMR CNRS 6230, University of Nantes) for their mass spectrometry analytical contributions to this work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: photocatalysis · hydrogen · alcohol oxidation · DSP systems

- [1] a) M. E. El-Khouly, E. El-Mohsawy, S. Fukuzumi, *J. Photochem. Photobiol. C* **2017**, *31*, 36–83; b) B. Zhang, L. Sun, *Chem. Soc. Rev.* **2019**, *48*, 2216–2264.
- [2] a) G. Reginato, L. Zani, M. Calamante, A. Mordini, A. Dessì, *Eur. J. Inorg. Chem.* **2020**, *2020*, 899–917; b) J. F. Huang, Y. Lei, T. Luo, J. M. Liu, *ChemSusChem* **2020**, *13*, 5863–5895; c) J. Willkomm, K. L. Orchard, A. Reynal, E. Pastor, J. R. Durrant, E. Reisner, *Chem. Soc. Rev.* **2016**, *45*, 9–23.
- [3] S. Bae, J. E. Jang, H. W. Lee, J. Ryu, *Eur. J. Inorg. Chem.* **2019**, *2019*, 2040–2057.
- [4] F. Wang, S. S. Stahl, *Acc. Chem. Res.* **2020**, *53*, 561–574.
- [5] a) H. Sterckx, B. Morel, B. U. Maes, *Angew. Chem. Int. Ed.* **2019**, *58*, 7946–7970; b) C. R. Lhermitte, K. Sivula, *ACS Catal.* **2019**, *9*, 2007–2017; c) Y. Xu, B. Zhang, *ChemElectroChem* **2019**, *6*, 3214–3226.
- [6] a) D. F. Bruggeman, T. M. Bakker, S. Mathew, J. N. Reek, *Chem. Eur. J.* **2021**, *27*, 218–221; b) S. Li, S. Kim, A. H. Davis, J. Zhuang, E. W. Shuler, D. Willinger, J.-J. Lee, W. Zheng, B. D. Sherman, C. G. Yoo, *ACS Catal.* **2021**, *11*, 3771–3781; c) E. Nikoloudakis, P. B. Pati, G. Charalambidis, D. S. Budkina, S. Diring, A. Planchat, D. Jacquemin, E. Vauthey, A. G. Coutsolelos, F. Odobel, *ACS Catal.* **2021**, *11*, 12075–12086; d) D. Bruggeman, S. Mathew, R. Detz, J. Reek, *Sustain. Energy Fuels* **2021**, *5*, 5707–5716; e) D. Antón-García, E. Edwardes Moore, M. A. Bajada, A. Eisenschmidt, A. R. Oliveira, I. A. Pereira, J. Warnan, E. Reisner, *Nat. Synth.* **2022**, *1*, 77–86; f) D. F. Bruggeman, A. A. Laporte, R. J. Detz, S. Mathew, J. N. Reek, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200175.
- [7] L. Zani, M. Melchionna, T. Montini, P. Fornasiero, *J. Phys. Energy* **2021**, *3*, 031001.
- [8] H. G. Cha, K.-S. Choi, *Nat. Chem.* **2015**, *7*, 328.
- [9] a) J. Warnan, L. Favereau, Y. Pellegrin, E. Blart, D. Jacquemin, F. Odobel, *J. Photochem. Photobiol. A* **2011**, *226*, 9–15; b) L. Favereau, J. Warnan, Y. Pellegrin, E. Blart, M. Boujita, D. Jacquemin, F. Odobel, *Chem. Commun.* **2013**, *49*, 8018–8020; c) T. W. Holcombe, J.-H. Yum, Y. Kim, K. Rakstys, M. Grätzel, *J. Mater. Chem. A* **2013**, *1*, 13978–13983; d) F. Zhang, K.-J. Jiang, J.-H. Huang, C.-C. Yu, S.-G. Li, M.-G. Chen, L.-M. Yang, Y.-L. Song, *J. Mater. Chem. A* **2013**, *1*, 4858–4863.
- [10] J. Warnan, J. Willkomm, J. N. Ng, R. Godin, S. Prantl, J. R. Durrant, E. Reisner, *Chem. Sci.* **2017**, *8*, 3070–3079.

- [11] L. Kavan, N. Tétreault, T. Moehl, M. Grätzel, *J. Phys. Chem. C* **2014**, *118*, 16408–16418.
- [12] K. S. Finnie, J. R. Bartlett, J. L. Woolfrey, *Langmuir* **1998**, *14*, 2744–2749.
- [13] E. Lam, M. Miller, S. Linley, R. R. Manuel, I. A. Pereira, E. Reisner, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215894.
- [14] a) L. Zhang, J. M. Cole, *ACS Appl. Mater. Interfaces* **2015**, *7*, 3427–3455; b) K. L. Materna, R. H. Crabtree, G. W. Brudvig, *Chem. Soc. Rev.* **2017**, *46*, 6099–6110.
- [15] A. Yamakata, T.-a. Ishibashi, H. Onishi, *Chem. Phys. Lett.* **2001**, *333*, 271–277.
- [16] F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant, E. Reisner, *Chem. Eur. J.* **2012**, *18*, 15464–15475.
- [17] J. E. Nutting, M. Rafiee, S. S. Stahl, *Chem. Rev.* **2018**, *118*, 4834–4885.
- [18] a) K. Hu, G. J. Meyer, *Langmuir* **2015**, *31*, 11164–11178; b) H.-Y. Chen, S. Ardo, *Nat. Chem.* **2018**, *10*, 17–23.
- [19] J. S. Beckwith, A. Aster, E. Vauthey, *Phys. Chem. Chem. Phys.* **2022**, *24*, 568–577.
- [20] B. Lang, S. Mosquera-Vázquez, D. Lovy, P. Sherin, V. Markovic, E. Vauthey, *Rev. Sci. Instrum.* **2013**, *84*, 073107.
- [21] M. Koch, R. Letrun, E. Vauthey, *J. Am. Chem. Soc.* **2014**, *136*, 4066–4074.
- [22] D. Cao, Q. Liu, W. Zeng, S. Han, J. Peng, S. Liu, *Macromolecules* **2006**, *39*, 8347–8355.
- [23] P. Brogdon, L. E. McNamara, A. Peddapuram, N. I. Hammer, J. H. Delcamp, *Synth. Met.* **2016**, *222*, 66–75.
- [24] L. Zhang, J. M. Cole, *J. Mater. Chem. A* **2017**, *5*, 19541–19559.
- [25] J. Humphreys, F. Pop, P. A. Hume, A. S. Murphy, W. Lewis, E. S. Davies, S. P. Argent, D. B. Amabilino, *CrystEngComm* **2021**, *23*, 1796–1814.
- [26] S. Nishioka, K. Hojo, D. Saito, I. Yamamoto, T. E. Mallouk, K. Maeda, *Appl. Catal. A* **2023**, *654*, 119086.
- [27] P. E. Hartnett, S. M. Dyar, E. A. Margulies, L. E. Shoer, A. W. Cook, S. W. Eaton, T. J. Marks, M. R. Wasielewski, *Chem. Sci.* **2015**, *6*, 402–411.

Manuscript received: December 12, 2023

Accepted manuscript online: January 16, 2024

Version of record online: February 12, 2024