Beyond Water Oxidation: Hybrid, Molecular-Based Photoanodes for the Production of Value-Added Organics

Mirco Natali1*, Andrea Sartorel2* and Albert Ruggi3*

1Department of Chemical Pharmaceutical and Agricultural Sciences (DOCPAS), University of Ferrara, Ferrara, Italy, 2Dipartimento di Scienze Chimiche, Università di Padova, Padova, Italy, 3Département de Chimie, Université de Fribourg, Fribourg, Switzerland

The political and environmental problems related to the massive use of fossil fuels prompted researchers to develop alternative strategies to obtain green and renewable fuels such as hydrogen. The light-driven water splitting process (i.e., the photochemical decomposition of water into hydrogen and oxygen) is one of the most investigated strategies to achieve this goal. However, the water oxidation reaction still constitutes a formidable challenge because of its kinetic and thermodynamic requirements. Recent research efforts have been focused on the exploration of alternative and more favorable oxidation processes, such as the oxidation of organic substrates, to obtain value-added products in addition to solar fuels. In this mini-review, some of the most intriguing and recent results are presented. In particular, attention is directed on hybrid photoanodes comprising molecular light-absorbing moieties (sensitizers) and catalysts grafted onto either mesoporous semiconductors or conductors. Such systems have been exploited so far for the photoelectrochemical oxidation of alcohols to aldehydes in the presence of suitable co-catalysts. Challenges and future perspectives are also briefly discussed, with special focus on the application of such hybrid molecular-based systems to more challenging reactions, such as the activation of C–H bonds.

Keywords: artificial photosynthesis, molecular sensitizer, solar fuels, value-added organics, hybrid photoanode

INTRODUCTION

Sunlight constitutes a virtually unlimited, widely available, and highly energetic resource. The utilization of solar energy to produce chemical fuels (e.g., hydrogen or CO₂ reduction products) is undoubtedly one of the most promising strategies to circumvent the intrinsic limitations of sunlight (Field et al., 1998; Balzani et al., 2008; Schultz and Yoon, 2014; Lewis, 2016). Most of the methods developed so far have been focused on the light-driven water splitting process: the utilization of sunlight to break the molecule of water into hydrogen and oxygen. Generally speaking, this process requires three components: a molecule capable of harvesting sunlight (sensitizer) and two catalysts suitable for performing the oxidation of water to oxygen and the reduction of protons to hydrogen (Concepcion et al., 2012). Extensive investigations lead to the development of several efficient systems for light-triggered hydrogen production (Mazzeo et al., 2021), whereas water oxidation still constitutes a bottleneck issue. In fact, water oxidation usually requires strongly oxidizing conditions, which often results in the degradation and consequent inactivation of the catalysts (Hong et al., 2013; Macchioni, 2019). Moreover, the water oxidation process is a four-electron/four-proton process with the formation of a new O–O bond and is thus associated with low kinetics. Eventually, molecular oxygen does not constitute an interesting product from the application viewpoint since it is widely...
available in the air (Inoue et al., 2011). To circumvent these issues, researchers have recently started to investigate the possibility of coupling proton reduction with other chemical reactions. More in detail, two main processes have been performed to achieve this goal: waste photoreforming and photoredox catalysis on pure organic substrates to obtain value-added products (Reisner, 2019; Toe et al., 2021; Kim et al., 2022). In photoreforming, the proton reduction reaction is coupled with the oxidation of organic substrates such as waste, plastics, and pollutants, with the formation of either CO₂ or value-added compounds (Cui et al., 2021; Luo et al., 2021). The main advantage of this strategy is the possibility of transforming environmentally harmful chemicals (which are costless and whose elimination is indeed a cost) into hydrogen and other fuels. However, the low solubility and/or the low concentration of the substrates pose a major kinetic challenge which constitutes the main drawback of this approach (Butburee et al., 2020; Nwosu et al., 2021; Toe et al., 2021; Uekert et al., 2021). Conversely, the coupling of proton reduction with photoredox catalysis aims at obtaining value-added organic products and fine chemicals starting from pure compounds such as alcohols, acids, aldehydes, and amines. Compared with photoreforming, photoredox catalysis requires pure starting materials, which might somehow reduce the cost-effectiveness of the process (Lhermitte and Sivula, 2019; Agosti et al., 2020; Tang and Sun, 2020; Qi et al., 2021). The vast majority of the systems reported so far both for photoreforming and photoredox catalysis are based on semiconductor nanoparticles, mostly used as suspensions. Several reviews

![Diagram](image-url)
Table 1: Relevant photoelectrochemical data of the systems discussed in Systems Based on Ruthenium Complexes section and Systems Based on Noble-Metal-Free and Organic Sensitizers section used in the oxidation of organic substrates.

| Substrate/product (reference) | J* (μA/cm²) | E (V) | IPCE (%) | FE (%) | Stability* (h) | Conditions |
|-------------------------------|-------------|-------|----------|--------|----------------|------------|
| Benzyl alcohol/benzaldehyde  | ~200        | 0.26f | 1 at 445 nm³ | 37     | n.d. | nanoITO/TiO₂, pH 4.5 |
| Benzyl alcohol/m.d.          | ~100        | 0.2   | n.d.     | n.d.   | n.d. | TiO₂, pH 4.6 |
| Phenol/m.d.                  | ~100        | 0.2   | n.d.     | n.d.   | n.d. | TiO₂, pH 4.6 |
| Benzyl alcohol/m.d.          | ~30         | 0.2   | n.d.     | n.d.   | n.d. | TiO₂, pH 4.35 |
| Phenol/1,2-benzquinoxaline   | ~70         | 0.2   | n.d.     | n.d.   | n.d. | TiO₂, pH 4.35 |
| 2-phenoxo-1-phenyl ethanol/2-phenoxo-1-phenylethanone | ~90 | 0.8f | n.d. | 91 | 80 | TiO₂, CH₃CN, NHPI/lutidine |
| Benzyl alcohol/benzaldehyde  | ~35         | 0.2   | n.d.     | n.d.   | 0.2 | core-shell SnO₂/TiO₂, pH 4.65 |
| 4-methoxybenzyl alcohol/methoxybenzyl aldehyde | ~180 | 0.45f | n.d. | 80f | 1 | Nano-ITO, pH 10 |

Organic and noble-metal-free based systems (Section 3):

| Substrate/product (reference) | J* (μA/cm²) | E (V) | IPCE (%) | FE (%) | Stability* (h) | Conditions |
|-------------------------------|-------------|-------|----------|--------|----------------|------------|
| 4-methoxybenzyl alcohol/4-methoxybenzyl aldehyde | 200 | 0.04f | 2.6 at 430 nm³ | 82f | 1.5 | TiO₂, pH 8 or CH₃CN/Melmtd. |
| Benzyl alcohol/benzaldehyde  | 400         | 0     | n.d.     | 100    | 32  | TiO₂, CH₃CN, TEMPO/LTFSI |
| 4-methylbenzyl alcohol/4-methylbenzaldehyde  | ~90         | –0.27f | 2 at 425 nm³ | 87f | 22 | TiO₂, pH 8 |
| Benzyl alcohol/m.d.          | 18          | 0.6   | n.d.     | 2      |    | ITO, CH₃CN, TEMPO. |
| Benzyl alcohol/m.d.          | ~90         | 0.4   | n.d.     | 2      |    | SnO₂, CH₃CN, NHS/ pyridine |

Abbreviations: NHPI = N-hydroxypyridinium, Melmd: N-methylimidazole, LTFSI = lithium bis(trifluoromethanesulfonyl)imide, NHS = N-hydroxysuccinimide, n.d. = not determined.
1*current density is expressed per geometric surface area;
2original bias referenced vs. Ag/AgCl for a direct comparison of the systems;
3indicative time of activity as reported in the publication;
4originally reported vs. NHE and converted according to the formula E (V, vs. Ag/AgCl) = E (V, vs. NHE)−0.2;
5estimated using the known APCE, the dye loading, and the resulting LHE;
6originally reported vs. SCE and converted according to the formula E (V, vs. Ag/AgCl) = E (V, vs. SCE) + 0.04V;
7reported turnover number (TON) = 151;
8reported TON = 26;
9reported TON = 131 ± 22 (STEMPO) and TON = 853 ± 107 (DPP-CA, see Figure 2 for the structures).

have been recently published on this subject and will not be discussed here (Kampouri and Stylianou, 2019; Qi et al., 2021; Yuan et al., 2021; Casadevall, 2022). Material-based systems, either used as suspensions or electrodes, usually yield better performing and easy-to-handle devices, although at the expense of a more challenging mechanistic investigation and component tailoring, which are typical properties of systems based on organic or coordination compounds (Berardi et al., 2014; Zhou et al., 2015; Zhang and Sun, 2019; Qi et al., 2021). Systems including molecular species grafted on semiconductors and immobilized on photoelectrodes (hybrid systems) enable the merging of the best of both strategies. Such architectures could play an important role in photoredox catalysis, exploiting the tunability and the straightforward mechanistic investigation of the molecular systems coupled with the stability of semiconductors (Hennessey and Farràs, 2018; Wu et al., 2018). The related main components and the basic mechanistic steps are shown in Figure 1A. A sensitizer anchored onto the electrode is used as the light-harvesting unit to initiate the redox processes via electron injection. A catalyst, either attached to the electrode or in the solution, is then used to receive the oxidizing equivalents from the oxidized sensitizer in a stepwise manner and perform the transformation of the substrate. Injected electrons are collected in a dark cathode to accomplish the fuel-forming reaction (e.g., hydrogen generation). This field of research is still in its infancy: the very few reports which have appeared so far constitute the object of this article. In this mini-review, we discuss in detail some selected examples of hybrid systems used in oxidative photoredox catalysis with the aim of drawing conclusions which could orient the community toward the development of more efficient solutions. The oxidation of alcohols was chosen as the target reaction since it has been widely explored in recent literature in conjunction with fuel-forming reactions, for example, hydrogen evolution. The selected systems provide examples of different architectures, separately discussed on the basis of the active components. These include Ru-based systems (Systems Based on Ruthenium Complexes section) and noble-metal-free ones (Systems Based on Noble-Metal-Free and Organic Sensitizers section) grafted on electrodes based on either nanocrystalline n-type inorganic semiconductors (TiO₂, SnO₂, or related core-shell systems) or mesoporous conductors such as nano-ITO (Eftekhar et al., 2017). For the sake of comparison, the main photoelectrochemical results are summarized in Table 1.
SYSTEMS BASED ON RUTHENIUM COMPLEXES

The idea of using heterogenized ruthenium-based molecular species to accomplish light-driven oxidation reactions was first reported in 1999 by T. J. Meyer et al., who synthesized a dyad (Figure 1B) featuring a ruthenium polypyridine chromophore coupled with a ruthenium oxidation catalyst through a 2,3-bis(2-pyridyl)-pyrazine (dpp) bridge (Treadway et al., 1999). When attached to nanocrystalline TiO₂, the dyad was capable of driving the conversion of 2-propanol to acetone on visible light irradiation with concomitant hydrogen evolution at the counter electrode. Although the performance of the system was not optimized (maximum current densities achieved were <1 μA/cm²), this work pioneered the use of heterogenized molecular components to perform oxidative organic transformation.

Following these premises, T. J. Meyer et al. reported the oxidation of benzyl alcohol using photoanodes based on either mesoporous TiO₂ or core-shell nano-ITO|TiO₂ nanoparticles functionalized with a chromophore and a catalyst based on ruthenium complexes (Figure 1C) (Song et al., 2014). Maximum photocurrent densities (J) of ~60 (+0.2 V vs. NHE applied bias) and ~200 μA/cm² (+0.4 V vs. NHE applied bias) were measured in the presence of 0.1 M benzyl alcohol for the TiO₂ and nano-ITO|TiO₂ photoanodes, respectively. An absorbed photon-to-current conversion efficiency (APCE) of 0.36 and 3.7% was recorded for the two photoanodes. The improved activity of the core-shell system was attributed to the decreased charge recombination with respect to the sole TiO₂. Photoelectrolysis experiments showed the formation of benzaldehyde as the oxidation product with Faradaic yields of 26 and 37% for the TiO₂ and nano-ITO|TiO₂ photoanodes, respectively. For these systems, the photo-oxidation reaction is mediated by high-valent RuIV=O species generated upon irradiation, after the electron injection of the chromophore unit into the oxide support and subsequent hole transfer to the catalyst. In a similar approach, Leem et al. prepared a polystyrene-based system comprising both ruthenium-based catalysts and sensitizers (Figure 1F) (Jiang et al., 2017). The deposition of such a polymeric assembly onto nanocrystalline TiO₂ leads to active photoanodes for the light-driven oxidation of phenol and benzyl alcohol. Under 1 Sun irradiation and on the application of a +0.2 V vs. Ag/AgCl potential bias, J in the order of ~10 μA/cm² were recorded in an acetate buffer solution at pH 4.65 in the presence of 0.1 M benzyl alcohol. Photocatalysis involves the electron injection of the dye onto TiO₂ upon photo-excitation followed by the proton-coupled oxidation of the NHPI in the solution to the N-oxyl PINO radical, which eventually promotes substrate conversion through a hydrogen atom transfer (HAT) mechanism. More interestingly, the hybrid system turns out to be effective in the photo-oxidation of natural lignin in the acetone solution, with measured J of ~130 μA/cm² under comparable experimental conditions. Odobel et al. reported the synthesis of a molecular triad based on a ruthenium tris (bipyridine) complex as the photosensitizer, connected on one side to the TEMPO alcohol oxidation catalyst and on the other side to a naphthalenediarylcarboxanhydride dicarboximide (NDADI) electron acceptor (Figure 1H) (Nikoloudakis et al., 2021). When attached onto nano-ITO, the triad effectively mediates the oxidation of para-methoxybenzyl alcohol in a pH 10 carbonate buffer solution on visible light irradiation at a bias of +0.4 V versus SCE. A maximum Faradaic efficiency of ~8% was recorded for the formation of para-methoxybenzaldehyde, suggesting the enhanced selectivity of the photocatalytic system. The system deactivates along 1 h photoelectrolysis due to partial leaching of the molecular triad from the ITO surface and the concomitant degradation of the ruthenium chromophore unit. Substrate activation occurs via electron transfer from the excited ruthenium dye to nano-ITO, likely mediated by the NDADI acceptor, followed by hole transfer to the TEMPO unit which promotes alcohol oxidation through a HAT mechanism, similar to the NHPI system previously discussed (Li et al., 2020).
SYSTEMS BASED ON NOBLE-METAL–FREE AND ORGANIC SENSITIZERS

Inspired by the natural photosystem II, porphyrinoid derivatives were considered viable alternatives to ruthenium polypyridine dyes in light-induced water oxidation cycles (Orbelli Birolì et al., 2019) and exploited in the design of photoanodes in combination with suitable catalysts (Moore et al., 2011; Poddutoori et al., 2015; Yamamoto et al., 2016).

The lower oxidation power required for the transformation of organics can open new opportunities for a plethora of porphyrin dyes which usually require ring functionalization to achieve potentials suitable for water oxidation. Within this framework, one elegant system was recently proposed by Odobel et al., combining a zinc porphyrin and a TEMPO catalyst onto a TiO2 semiconductor (Figure 2A) (Nikoloudakis et al., 2021). The system was successfully applied in the photoelectrochemical oxidation of benzyl alcohol derivatives in the presence of methyl imidazole as the base, with better performances observed in aqueous borate buffer with respect to the acetonitrile solution. J ~ 200 μA/cm² was observed at pH 8 at 0 V versus SCE, associated with a Faradaic yield of ~82% for benzyl alcohol oxidation along a 2-h photo electrolysis. The incident photon-to-current conversion efficiency (IPCE) reached 2.6% at 430 nm, in correspondence with the Soret absorption. Transient absorption studies confirmed an ultrafast electron injection of the excited Zn porphyrin into the TiO2 conduction band with the formation of the porphyrin radical cation. A slow TEMPO→ZnPor⁺ electron transfer then occurs in the hybrid material, only partially competing with recombination, consistent with the low driving force for the process (0.1 eV) and the poor electronic coupling between the units. Interestingly, similar photoelectrochemical performances were also obtained by adding the TEMPO catalyst in a homogenous solution, avoiding the synthetic effort to bind it to the porphyrin chromophore. The aspect of heterogenizing the TEMPO catalyst for alcohol oxidation was also discussed by Reek et al. (Bruggeman et al., 2021a; Bruggeman et al., 2021b), in the development of photoanodes sensitized with thienopyrroledione-based organic dye (AP11, Figure 2B). The AP11 dye can be efficiently chemisorbed onto TiO2, and electron injection from the excited state is energetically favorable by 0.3 eV. The AP11+/AP11 couple is characterized by a high oxidizing power (E = +1.80 V vs. NHE) and can promote the oxidation of TEMPO.

Under optimized conditions, the photoelectrochemical systems are active toward the oxidation of benzyl alcohol to benzaldehyde with an almost quantitative Faradaic efficiency, characterized by J up to 400 μA/cm² at 0 V versus Ag/AgCl, stable for up to 32 h at 50 mW/cm² irradiation, although high concentrations of TEMPO and lithium bis(trifluoromethanesulfonyl)imide as a base were required (1.0 and 1.2 M, respectively, in acetonitrile) (Bruggeman et al., 2021a). To overcome this drawback, the authors proposed to anchor the TEMPO catalyst onto the TiO2 layer by exploiting a silatrane linker (Bruggeman et al., 2021b). However, the system performed worse (i.e., an order of magnitude lower J and a decreased stability) with respect to the one keeping TEMPO in the solution. The authors attributed the poor performance of the integrated dye/catalyst photoanodes to inefficient hole migration from the oxidized form of the dye to the TEMPO catalyst and to...
recombination events involving back-electron transfer from TiO₂ to oxidized TEMPO® species at the surface. A similar “fully heterogenous” approach was recently developed by Warnan and Reisner by chemisorbing diketopyrrolopyrrole dyes (through carboxylic or phosphonic acid anchoring groups) and a TEMPO catalyst onto TiO₂ (Figure 2C (Antón-García et al., 2022)). Importantly, the dyes were designed for localizing the LUMO in the proximity of the anchoring group, thus favoring electron injection into the semiconductor. The photoanodes reached J up to ~90 μA/cm² for oxidation of 4-methyl-benzyl alcohol in borate buffer (pH 8) when applying +0.4 V versus RHE, with Faradaic yields in the range 80–100% and 60–90% when using the carboxylic and phosphonic anchoring groups, respectively. Under these conditions, the IPCE reached 2% at 425 nm and the electrodes showed good stability, retaining 50% of the activity after 12 h. Interestingly, a similar efficiency was also observed for the oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran (J up to ~70 μA/cm²) with 50% of the activity after 12 h. Interestingly, a similar efficiency was also observed for the oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran (J up to ~70 μA/cm²) with 50% of the activity after 12 h.

Other organic dyes that were considered in the photoanodes for alcohol oxidations are perylene (onto ITO) (Zhuang et al., 2020) and polyquinoid Ku-quinone (onto mesoporous SnO₂) (Volpato et al., 2021) (Figures 2D,E, respectively), taking inspiration from previous reports on photoelectrochemical water oxidation (Ronconi et al., 2015; Kirner and Finke, 2017; Bonchio et al., 2019; Volpato et al., 2020). In both cases, the systems were proposed for the oxidation of benzyl alcohol in the presence of a redox mediator and a base in the acetoni trile solution, reaching J of 18 and 90 μA/cm², respectively. In the case of the Ku-quinone dye, it is worth mentioning the high oxidative power of the excited state (>2 V vs. NHE) that drives the direct oxidation of the species in the solution followed by electron injection into the semiconductor from its radical anion, which was characterized by transient spectroscopy (Volpato et al., 2020; Volpato et al., 2021). In this case, the ability of the dye to exchange protons in concomitance with electrons could open a new perspective by offering the possibility of performing the photoelectrochemical oxidation of alcohols in the absence of a catalyst, thus enlarging the arsenal of organic dyes usable in the design of photoanodes for selective oxidation.

CONCLUSION AND FUTURE PERSPECTIVES

The systems presented in this mini-review demonstrate the great potential of hybrid molecular-based photoanodes when applied to photoredox reactions to replace water oxidation in the production of solar fuels. While the research in this field was pioneered with Ru-based photosensitizers, recent contributions have demonstrated the great potential of noble metal–free and organic photosensitizers. Because of milder operative conditions required with respect to photoelectrochemical water oxidation, it is expected that the pool of organic photosensitizers for such applications will enlarge soon. Considering the scarcity and cost of ruthenium, this observation is particularly encouraging, although definitive conclusions cannot be drawn because of the very limited number of systems reported so far. Almost all discussed systems require an externally applied bias, which has to be provided from external energy sources. Thus, the development of more active and stable sensitizers and unbiased systems (e.g., via tandem approaches) will probably constitute the development of this field in the near future. The biggest challenge, however, is probably the application of these systems to more attractive reactions, such as the selective oxidative activation of C–H bonds. So far, these processes have been pioneered with semiconductor-based photoanodes such as BiVO₄ (Li et al., 2017) and WO₃ (Tateno et al., 2018), and for the oxidation of benzyl C–H in tetralin and of aliphatic C–H bonds in cyclohexane. In this regard, molecular components offer the possibility to tune the system according to the mechanistic requirement of the target transformation. Molecular photocatalysts have been already proposed for the homogenous hydroxylation of aromatic C–H, proceeding via one-electron oxidation of the aromatic ring followed by water insertion (Fukuzumi et al., 2019). However, for inactivated aliphatic C–H bonds, the one-electron oxidation usually requires high potentials (>2.5 V vs. SCE) (Baran 2017). Therefore, hydroxylation of such C–H bonds should consider more favorable pathways through a formal hydrogen atom abstraction as the first step, where the bond dissociation free energy (BDFE) should be considered the key descriptor of reactivity (BDFE of C–H bonds stands in the range 70–110 kcal/mol, (Agarwal et al., 2022)). Within this scenario, the use of transition metal catalysts enabling the formation of high-valent metal-oxo species could be envisaged.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

FUNDING

Financial support was provided by Italian MUR (PRIN project 2020927WY3 “ElectroLight4Value,” MN), Fondazione Cariparo (project Synergy, ricerca scientifica di eccellenza 2018, AS), and by the Swiss National Foundation (Grant 200021 159716, AR).

ACKNOWLEDGMENTS

We thank the talented and passionate students who have conducted research in our groups.
Qi, M.-Y., Conte, M., Anpo, M., Tang, Z.-R., and Xu, Y.-J. (2021). Cooperative Coupling of Oxidative Organic Synthesis and Hydrogen Production over Semiconductor-Based Photocatalysts. *Chem. Rev.* 121 (21), 13051–13085. doi:10.1021/acs.chemrev.1c00197

Reisner, E. (2019). When Does Organic Photoredox Catalysis Meet Artificial Photosynthesis? *Angew. Chem. Int. Ed.* 58 (12), 3656–3657. doi:10.1002/anie.201814692

Ronconi, F., Syrgiannis, Z., Bonasera, A., Prato, M., Argazzi, R., Caramori, S., et al. (2015). Modification of Nanocrystalline WO3 with a Dicaticionic Perylene Bisimide: Applications to Molecular Level Solar Water Splitting. *J. Am. Chem. Soc.* 137 (14), 4630–4633. doi:10.1021/jacs.5b01519

Schultz, D. M., and Yoon, T. P. (2014). Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* 343 (6174), 1239176. doi:10.1126/science.1239176

Song, W., Vannucci, A. K., Farnum, B. H., Lapides, A. M., Brennan, M. K., Kalanyan, B., et al. (2014). Visible Light Driven Benzyl Alcohol Dehydrogenation in a Dye-Sensitized Photocatalysis Cell. *J. Am. Chem. Soc.* 136 (27), 9773–9779. doi:10.1021/ja505022f

Tang, J.-H., and Sun, Y. (2020). Visible-light-driven Organic Transformations Integrated with H2 Production on Semiconductors. *Mat. Adv.* 1 (7), 2155–2162. doi:10.1039/D0MA00327A

Tateno, H., Iguchi, S., Miseki, Y., and Sayama, K. (2018). Photoelectrochemical C–H Bond Activation of Cyclohexane using a WO3 Photoanode and Visible Light. *Angew. Chem. Int. Ed.* 57 (35), 11238–11241. doi:10.1002/anie.201805079

Toe, C. Y., Tsounis, C., Zhang, J., Masood, H., Gunawan, D., Scott, J., et al. (2021). Advancing Photoreforming of Organics: Highlights on Photocatalyst and System Designs for Selective Oxidation Reactions. *Energy Environ. Sci.* 14 (3), 1140–1175. doi:10.1039/D0EE03116f

Treadway, J. A., Moss, J. A., and Meyer, T. J. (1999). Visible Region Photocatalysis on TiO2 with a Chromophore–Catalyst Molecular Assembly. *Inorg. Chem.* 38 (20), 4386–4387. doi:10.1021/ic990466m

Uekert, T., Pichtler, C. M., Schubert, T., and Reisner, E. (2021). Solar-driven Reforming of Solid Waste for a Sustainable Future. *Nat. Sustain.* 4 (5), 383–391. doi:10.1038/s41893-020-00650-x

Volpato, G. A., Colusso, E., Paoloni, L., Forchetta, M., Sgarbossa, F., Cristino, V., et al. (2021). Artificial Photosynthesis: Photocatalysts Based on Polyquinoid Dyes onto Mesoporous Tin Oxide Surface. *Photochem. Photobiol. Sci.* 20 (10), 1243–1255. doi:10.1039/d0pp00222f

Volpato, G. A., Marasi, M., Gobbato, T., Valentini, F., Sabuzi, F., Gagliardi, V., et al. (2020). Photoanodes for Water Oxidation with Visible Light Based on a Pentacyclic Quinoid Organic Dye Enabling Proton-Coupled Electron Transfer. *Chem. Commun.* 56 (15), 2248–2251. doi:10.1039/C9CC09805D

Wu, H.-L., Li, X.-B., Tung, C.-H., and Wu, L.-Z. (2018). Recent Advances in Sensitized Photocathodes: From Molecular Dyes to Semiconducting Quantum Dots. *Adv. Sci.* 5 (4), 1700684. doi:10.1002/advs.201700684

Yamamoto, M., Nishizawa, Y., Chábera, P., Li, F., Pascher, T., Sundström, V., et al. (2016). Visible Light-Driven Water Oxidation with a Subporphyrin Sensitizer and a Water Oxidation Catalyst. *Chem. Commun.* 52 (94), 13702–13705. doi:10.1039/C6CC07877J

Yuan, Y., Jin, N., Sagh, P., Dube, I., Zhu, H., and Chen, O. (2021). Quantum Dot Photocatalysts for Organic Transformations. *J. Phys. Chem. Lett.* 12 (30), 7180–7193. doi:10.1021/acs.jpclett.1c01717

Zhang, R., and Sun, L. (2019). Artificial Photosynthesis: Opportunities and Challenges of Molecular Photocatalysts. *Chem. Soc. Rev.* 48 (7), 2216–2264. doi:10.1039/C8CS00897C

Zhou, X., Li, F., Li, X., Li, H., Wang, Y., and Sun, L. (2015). Photocatalytic Oxidation of Organic Compounds in a Hybrid System Composed of a Molecular Catalyst and Visible Light-Absorbing Semiconductor. *Dalton Trans.* 44 (2), 475–479. doi:10.1039/C4DT02945C

Zhuang, J.-L., Shen, Y.-M., Xue, Y., Yan, M., Cheng, H., Chen, Z., et al. (2020). Electrochemical Deposition of Perylene-Based Thin Films from Aqueous Solution and Studies of Visible-Light-Driven Oxidation of Alcohols. *ACS Appl. Energy Mat.* 3 (9), 9096–9106. doi:10.1021/acsaeem.0c01475

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's Note: All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2022 Natali, Sartorel and Ruggi. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.