RSC Advances

REVIEW

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2024, **14**, 2590

Novel applications of photobiocatalysts in chemical transformations

Praveen P. Singh,[a] Surabhi Sinha,[a] Pankaj Nainwal,[b] Pravin K. Singh[c] and Vishal Srivastava *[c]

Received 29th October 2023
Accepted 28th December 2023

DOI: 10.1039/d3ra07371h

rsc.li/rsc-advances

Photocatalysis has proven to be an effective approach for the production of reactive intermediates under moderate reaction conditions. The possibility for the green synthesis of high-value compounds using the synergy of photocatalysis and biocatalysis, benefiting from the selectivity of enzymes and the reactivity of photocatalysts, has drawn growing interest. Mechanistic investigations, substrate analyses, and photobiocatalytic chemical transformations will all be incorporated in this review. We seek to shed light on upcoming synthetic opportunities in the field by precisely describing mechanistically unique techniques in photobiocatalytic chemistry.

1. Introduction

Considering that it is secure to use and easily accessible, light is the ideal energy source for environmentally friendly chemical synthesis.[1] The leading scientist Ciamician presented his ideas in the lecture "Photochemistry of the Future" in 1912, and predicted that sunlight, a plentiful and renewable source, could be used to create compounds in a manner similar to plants and that solar energy in organic synthesis had a lot of potential.[2–4]

Photocatalysis and biocatalysis (photobiocatalysis)[5–10] have attracted a lot of attention in the field of catalysis due to features that make these chemical synthesis methods more effective and environmentally sustainable. As enzymes may facilitate complex processes with excellent stereoselectivity and efficiency in water-based media at room temperature, the pharmaceutical and chemical industries have adopted biocatalysts in growing numbers as tools for green chemistry.[11–14] In contrast, photocatalysis has become a potent method that uses visible light excitation to reach particular reactivities, *via* the formation of open-shell intermediates, that are inaccessible *via* thermal activation modes. While in the past organic compounds were directly activated using ultraviolet (UV) light, modern photochemical activation approaches depend on the selective excitation of photocatalysts with visible light and can prevent the harmful destruction of organic

[a]*Department of Chemistry, United College of Engineering & Research, Prayagraj, U. P.-211010, India. E-mail: ppsingh23@gmail.com*
[b]*School of Pharmacy, Graphic Era Hill University, Dehradun, Uttarakhand, India*
[c]*Department of Chemistry, CMP Degree College, University of Allahabad, Prayagraj, U. P.-211002, India. E-mail: vishalgreenchem@gmail.com*

Praveen P. Singh

Praveen P. Singh is an Assistant Professor in the Department of Chemistry at the United College of Engineering and Research, Prayagraj, India. He obtained his BSc and MSc degrees in Organic Chemistry from T. D. P. G. College (V. B. S. Purvanchal University) Jaunpur and his DPhil. from the Department of Chemistry, University of Allahabad, India. His current research interests include the development of synthetic receptors for the recognition of biological target structures and the application of visible light chemical photocatalysis towards organic synthesis as well as nanophotocatalysis.

Surabhi Sinha

Surabhi Sinha is presently working as an Assistant Professor in the Department of Chemistry, United College of Engineering & Research, Naini, Prayagraj. She completed her graduate and post-graduate studies and DPhil. at the University of Allahabad, Prayagraj. Her research interests mainly include quaternary complexes of biochemical significance and organic synthetic transformations. She is a life member of several professional bodies.

molecules brought on by using high-energy UV light. Through the conversion of photonic energy into chemical energy, visible light-mediated photocatalysis offers a gentle, long-lasting, and clean technique for chemical activation and has been utilised to facilitate numerous challenging transformations.[15–21]

Replicability and reproducibility challenges are frequently raised by researchers in novel fields of research, including in photobiocatalysis. Studies are often conducted by a select group of laboratories utilising their own in-house solutions to run and investigate reactions. It is therefore vital to provide criteria for reporting the technical and chemical specifics of photobiocatalytic reactions as the subject advances to broader applicability. Since these guidelines have been shown to be significant for both biocatalysis and photocatalysis, we emphasise here the characteristics that are particularly relevant to photobiocatalysis (Fig. 1).[22]

Photobiocatalysis makes use of excellent enzyme selectivity and the distinctive chemical changes that photocatalysis is capable of to carry out chemical transformations (Fig. 2).[23–26] Because enzymes are highly evolved for specific biological functions, their limited synthetic potential can be addressed by providing them with additional reactivity by using photoactive cofactors like flavin or nicotinamide adenine dinucleotide (phosphate) (NAD(P)H) or photocatalysts like ruthenium and iridium organometallic complexes, organic dyes, *etc.*[27,28] The protein framework of enzymes, in turn, can provide a regulated environment that provides possibilities to direct reactive intermediates toward the required stereo- and chemo-selective outcome, a current issue for conventional photocatalysts.[29] The problems of compatibility between enzymes and photocatalysts which arise because they both work under different reaction conditions and the kinetics of the photogenerated reactive intermediates and enzyme catalysis are obstacles to merging the two types of catalysis. Furthermore, it is difficult to employ protein engineering techniques for the improvement of photoenzymatic systems due to the challenges in achieving uniform illumination and an inert atmosphere for a significant amount of samples.[30,31]

The rapidly expanding field of photobiocatalysis is devoted to the creation of novel light-dependent biocatalytic processes.[32–37] The link between the photochemical process and the enzymatic transformation will be used to group reports in this evaluation. We will clarify crucial terms and concentrate on subtle mechanistic differences that set several techniques apart from one another. We aim to add to the understanding of how light can be employed in biocatalytic synthesis by describing the mechanistic differences between various techniques.

The first technique focuses mostly on photoenzymatic catalysis, where a cofactor inside a protein active site is photoexcited, it facilitates the electron or energy transfer necessary to change a starting material into a finished product (Fig. 3a). Synergistic photoenzymatic catalysis is addressed in the second approach (Fig. 3b). In these processes, an external cofactor is excited to enable a chemical change within a protein active site. The third procedure incorporates tandem photocatalyst/enzyme reactions (Fig. 3c). In these *trans*-formations, the photochemical reaction takes place in the presence of the enzyme but is not a part of the mechanism by which the enzyme transforms raw materials into the end products. This procedure is further divided into (i), processes that use light to regenerate cofactors and (ii), reactions where the enzyme substrate is altered by photoexcitation. The fourth method addresses natural photosynthesis and enzymatic processes. Through the utilisation of cyanobacteria, these

Pankaj Nainwal

Dr Pankaj Nainwal is a Professor in the School of Pharmacy, Graphic Era Hill University, Dehradun, Uttarakhand. He is an alumni of the JSS College of Pharmacy, Ootacmund, Tamil Nadu. During his academic journey he has taught in universities in various states. He specializes in pharmacognosy, phytochemistry, phytopharmacy, phytomedicines and photocatalysis.

Pravin K. Singh

Pravin K. Singh is an Assistant Professor at the Department of Chemistry, C. M. P. College, Allahabad, India (Constituent P. G. College of Central University of Allahabad). Dr Singh is actively engaged in advanced research work for the development of environmentally benign, new synthetic routes for various bioactive heterocyclic compounds. He completed his BSc, MSc, doctorate (DPhil.) and post-doctorate (DSc) studies at the University of Allahabad, India.

Vishal Srivastava

Vishal Srivastava is an Assistant Professor in the Department of Chemistry, C. M. P. College, (Constituent P. G. College of Central University of Allahabad) Prayagraj, India. He completed his graduate (BSc) and post-graduate (MSc) studies and his doctoral degree (DPhil.) in organic chemistry at the Department of Chemistry, University of Allahabad, India. His current research work involves the design of novel biologically active photoredox catalysed synthetic organic compounds.

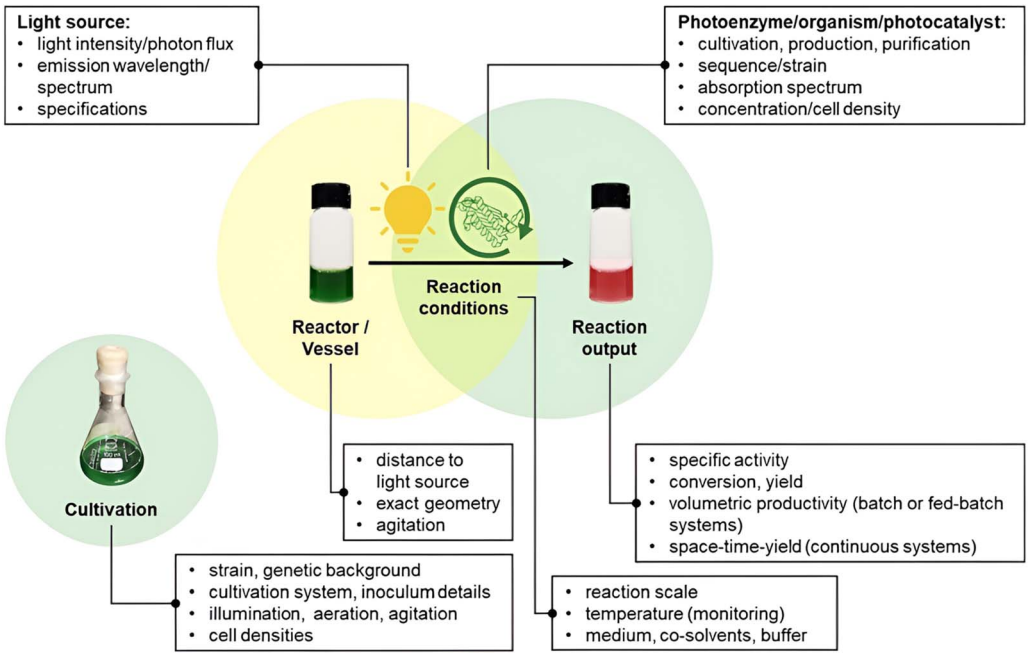


Fig. 1 General criteria for reporting photobiocatalytic reactions. Reproduced with permission from ref. 22. Copyright © 2023 The Authors. ChemPhotoChem published by Wiley-VCH GmbH.

systems generate NADPH, which enzymes can use to reduce substrates (Fig. 3d). This concise review deals with photobiocatalysis as an effective method in energy production and chemical manufacture and is a follow-up to our work on photocatalyzed organic synthesis,[38,39] paying particular attention to the most recent and noteworthy developments in this field. Those already working in the field of photoredox catalysed synthesis and interested in the usage of photobiocatalysis-driven chemical and energy production may find this review to be particularly useful.

2. Applications of photobiocatalysts in chemical transformations

2.1. Photobiocatalytic H_2 production

The long-term goal of researchers and a potential remedy for energy problems, environmental degradation, and global warming is to transform renewable solar energy into fuels and value-added chemicals. In order to efficiently capture and store solar energy in chemical bonds, photosynthetic biohybrid systems (PBS) can utilise both artificial semiconductor materials with high solar conversion efficiency and living cells with high product selectivity.[40]

An intriguing approach for producing H_2 has been established through photobiocatalysis. Kosem *et al.*[41] have examined the natural properties of biocatalysts and the significance of each component in determining the effectiveness of the system. Tris (2-amino-2-hydroxymethyl-1,3-propanediol) was shown *via* photocatalytic research to be the optimal electron donor for the reduction of viologen by TiO_2 (Scheme 1). A study of the biocatalytic reaction showed that the function of the whole-cell biocatalysts was strongly influenced by cell permeability, the redox potential of the electron mediators, and the cell envelope. Recombinant *Escherichia coli*, which has a turnover frequency of

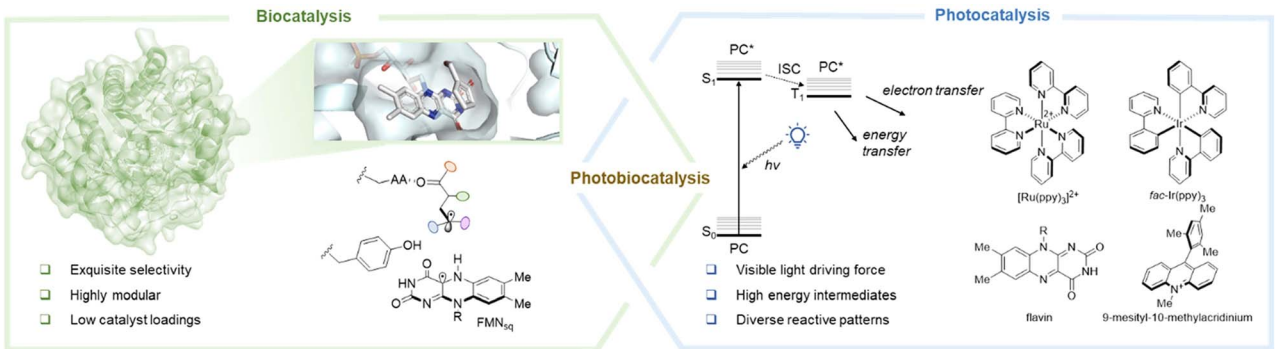


Fig. 2 In the presence of light, the combination of photocatalysis and biocatalysis simplifies challenging reactions. Photocatalyst = PC; S_0 = singlet ground state; S_1 = first singlet excited state; T_1 = first triplet excited state; FMNsq = semiquinoneflavin mononucleotide. Reproduced with permission from ref. 26. Copyright © 2022 American Chemical Society.

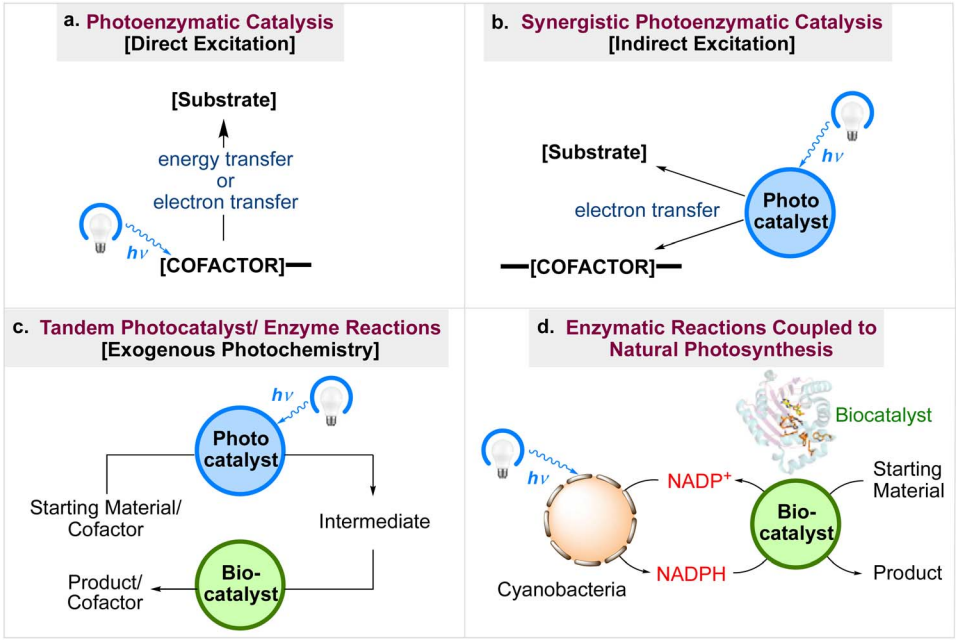


Fig. 3 Types of photobiocatalysis used in chemical transformations.[34]

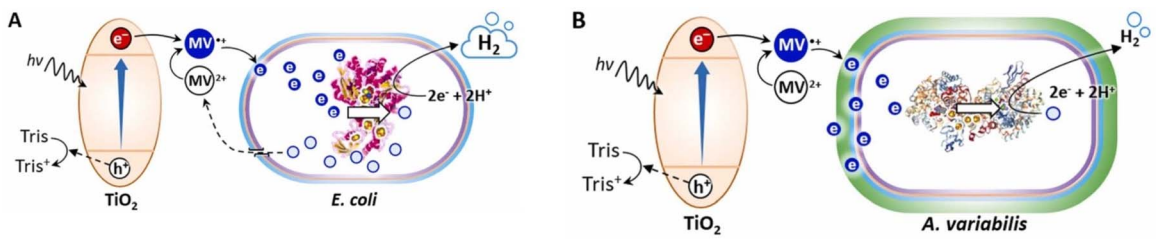
39.43 3.77 s^{-1} based on [FeFe]-hydrogenase activity, was illustrated to be a more effective biocatalyst than Anabaena variabilis in a photobiocatalytic system. A thorough investigation revealed that Tris and MV^{2+} had less of an impact on H_2 synthesis than TiO_2, light, and the biocatalysts. With a solar-to-H_2 conversion of 1.58 (0.10%), a maximum rate of 16.73 1.03 mol min^{-1} was achieved. The production of highly effective photobiocatalysts will be guided by an understanding of the functions of each component. Table 1 provides information on the capabilities of hydrogen evolution photobiocatalytic systems, including relative H_2 yield (to bare cells) and endurance.

2.2. Photobiocatalytic CO_2 reduction and conversion

A promising technique to address climate challenges and store solar energy is the conversion of CO_2 into value-added compounds utilising renewable solar energy as the driving force. In addition, when compared to the conversion of solar energy to hydrogen, the conversion of solar energy to organic molecules has the advantage of the products being easy to transport and store.[57–65] The descriptions of the capabilities of the photobiocatalytic CO_2 conversion systems are given in Table 2. The mechanism[66a,b] by which the production of CO_2RR by photocatalysis proceeds is given in Scheme 2.

2.3. Coordination of electron transfer and enzyme protection

In order to coordinate electron transmission and enzyme protection for photo-enzymatic alcohol synthesis, Jiang and colleagues reported[78] a metal hydride-embedded titania (MH/TiO_2) coating that is engineered on graphitic carbon nitride (GCN). The MH/TiO_2 coating serves two essential functions: (1) it prevents the GCN core and coating from deactivating alcohol dehydrogenase (ADH); and (2) it allows electron transfer from GCN to nicotinamide adenine dinucleotide (NAD^+) and then to the alcohol dehydrogenase-catalyzed form of formaldehyde. The coordinated photo-enzymatic system was able to create methanol at a rate of 1.78 0.21 mol min^{-1} $mg_{(ADH)}^{-1}$, which is 420% more than the rate of the system made up of ADH and GCN without the coating. Additionally, the coordinated system is capable of producing methanol constantly for a minimum of three light–dark cycles, whereas the GCN and ADH system entirely shuts down after one light–dark cycle. By combining



Scheme 1 In the presence of Tris as a sacrificial agent and MV^{2+} as an electron mediator, a TiO_2 photobiocatalytic H_2 generation mechanism was coupled to two distinct whole-cell biocatalysts: recombinant *E. coli* (A) or the cyanobacterium *A. variabilis* (B). Reproduced with permission from ref. 41. Copyright © 2023 Elsevier.

Table 1 Summary of the performance of hydrogen evolution photobiocatalytic systems, including relative H_2 yield (to bare cells) and duration

Species	Photosensitizer	Efficiency/yield[a]	Relative H_2 yield to bare cells	Duration	Ref.
Azotobactervinelandii	CdS–ZnS quantum dots	AQE[a] 13%	NA	2 h	42
Desulfovibriodesulfuricans	CdS, methyl viologen	AQE 23%	NA	50 h	43
Desulfovibriodesulfuricans	CdS	AQE 4%	NA	10 d	43
Escherichia coli	TiO_2	AQE 0.31%	NA	15 h	44
Escherichia coli	CdS	AQE 7.93%	1.3 fold	3 h	45
Escherichia coli	$AgInS_2/In_2S_3$	AQE 3.3%	1.3 fold	3 h	46
Escherichia coli	CdS	Yield 81 μmol/10^8 cells	10 fold	24 h	47
Escherichia coli	TiO_2	Yield 3.6 mmol per mmol glucose	2.8 fold	15 h	48
Escherichia coli	Eosin Y	AQE > 10%	>10 fold	24 h	49
Escherichia coli	Iodine-doped hydrothermally carbonized carbon	AQE 9.11%	1.57 fold	3 h	50
Klebsiella pneumonia	Hydrothermal carbonation carbon	Yield 1020 μmol	1.35 fold	3 h	51
Rhodopseudomonaspalustris	CdS nanoparticles	Photosynthetic efficiency 6.73%	2 fold	120 h	52
Rhodopseudomonaspalustris	Oligofluorene, polythiophene	Yield 1250 nmol	~1.67 fold	2 h	53
Shewanellaoneidensis	Eosin Y	AQE 0.6%	>10 fold	24 h	54
Shewanellaoneidensis	Cu_2O, reduced graphene oxide	Yield 322 μmol per g Cu_2O	>10 fold	4 h	55
Shewanellaoneidensis	$CuInS_2$/ZnS quantum dots	AQE 15.02%	10 fold	45 h	56

[a] The apparent quantum efficiency (AQE) of a light-driven H_2 production system is the number of additional evolved H_2 molecules multiplied by 2 and divided by the number of incident photons.

synthetic and biological modules for solar chemical-based conversion, this study reveals the potential of redox-active mineral coverings (Scheme 3).

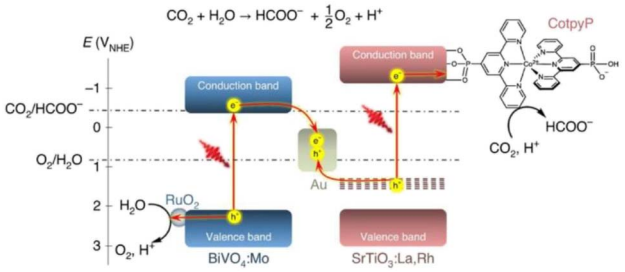
2.4. Photobiocatalytic conversion of proteomembranes into artificial chloroplasts

By employing inverted *E. coli* vesicles and heterodinuclear tpphz-bridged Ru–Rh photocatalysts, Rau *et al.* presented[79] a hybrid system that can concurrently produce the two physiologically active cofactors NADH and ATP while drawing energy from an external source, such as visible light. Thus, it mimics how natural chloroplasts work, which is to produce reduced nicotinamides and ATP for subsequent energy-demanding reductive cascade reactions. It was discovered by investigating the various ATP synthesis steps that the photocatalytically produced NADH actually acidifies the inside of the proteomembrane vesicles. The phosphorylation of glucose ultimately results from the usage of the resultant pmf,

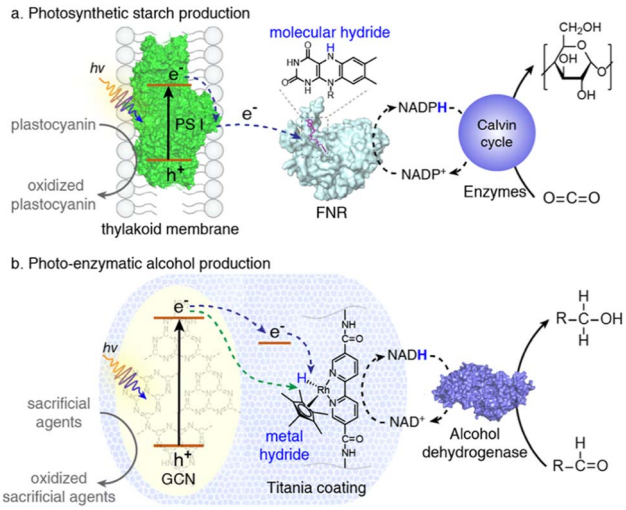
Table 2 Summary of the performance of photobiocatalytic CO_2 conversion systems

Species	Materials	Products	Efficiency/yield	Duration	Ref.
Azotobactervinelandii	CdS/ZnS QDs	Formic acid	Turnover number 10^6	NA	42
Cupriavidusnecator	CdS/ZnS QDs	C_2H_4, isopropanol, 2,3-butanediol, C_{11}–C_{15} methyl ketones, polyhydroxybutyrate	Turnover number 10^6–10^8	NA	42
Escherichia coli	CdS	L-Malate and butyrate	L-Malate yield = 1.48 mol per mol glucose Butyrate yield = 0.79 mol per mol glucose	4 days	67
Methanosarcinabarkeri	CdS	Methane	AQE[a] = 0.34%	5 days	68
Methanosarcinabarkeri	Ni:CdS	Methane	AQE = 2.08%	6 days	69
Moorellathermoacetica	PDI/PFP	Acetic acid	AQE = 1.6%	3 days	70
Moorellathermoacetica	CdS	Acetic acid	AQE = 2.44%	4 days	71
Moorellathermoacetica	CdS NPs, TiO_2–Mn phthalocyanine	Acetic acid	Yield ~1.2 mM	3.5 days	72
Moorellathermoacetica	Au NC	Acetic acid	AQE = 2.86%	7 days	73
Moorellathermoacetica	Au NC, alginate	Acetic acid	Yield ~ 1.4 mM	3 days	74
Rhodopseudomonaspalustris	CdS QDs	Methane	Yield ~171 nmol per mg total protein	4 days	75
Rhodopseudomonaspalustris	CdS NPs	Carotenoid, PHB	Photosynthetic efficiency 5.98%	8 days	76
Sporomusaovata	Silicon nanowire	Acetate	AQE = 3.6%	7 days	77

[a] The apparent quantum efficiency (AQE) refers to the ratio of electrons used to convert the substrate to product and the incident photons.



Scheme 2 An energy diagram depicting photosynthetic CO_2RR production coupled with water oxidation. The reduction potentials are given *versus* the NHE at pH 6.7. Reproduced with permission from ref. 66*a*. Copyright 2020 Springer Nature Publishing AG.

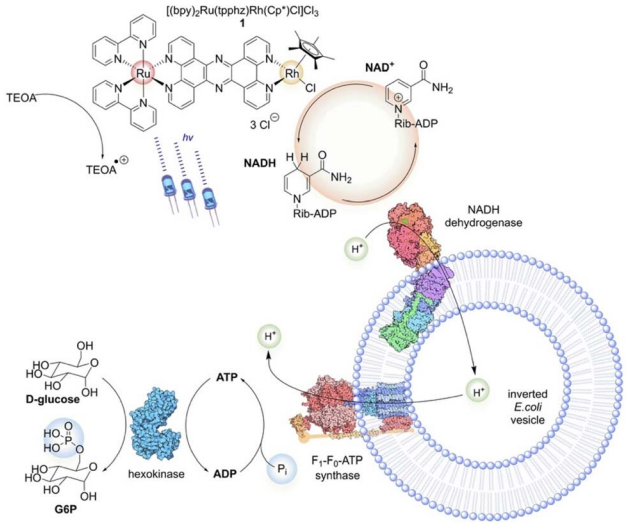


Scheme 3 (a) Production of photosynthetic starch using a thylakoid membrane and FNR with molecular hydride integration. (b) MH-embedded TiO_2 layer for photo-enzymatic alcohol synthesis. Reproduced with permission from ref. 78. Copyright © 2020 American Chemical Society.

transforming ADP and P_i into ATP. In green plants, photochemically generated ATP is used in a biochemically comparable phosphorylation reaction to activate ribulose-5-phosphate for CO_2 fixation and reduction. Thus, the final step of the studied reaction is also similar to the natural chloroplast system. Additionally, it was discovered that the overall charge and lipophilicity of the coordination compounds can influence how the examined Ru polypyridine complexes interact with the *E. coli*-generated vesicles. These findings pave the way for more applications, such as chain reactions using both the cofactors ATP and NADH. If appropriate enzymes were added to the cofactor-producing inorganic–biologic hybrid system indicated, energy-intensive reductive activations of N_2, as well as CO_2 fixation processes would be feasible (Scheme 4).

2.5. Morpholine-based buffers that activate aerobic photobiocatalysis

According to the findings of Gonçalves *et al.*,[80] morpholine-based buffers, particularly 3-(*N*-morpholino)propanesulfonic



Scheme 4 An illustration of the photobiocatalytic process that uses inverted *E. coli* vesicles as the main cofactor conversion machinery to connect the photocatalytic NADH generation by **1** with enzymatic ATP and G6P production. Reproduced with permission from ref. 79. Copyright © 2021 The Authors. *Angewandte Chemie International Edition* published by Wiley-VCH GmbH.

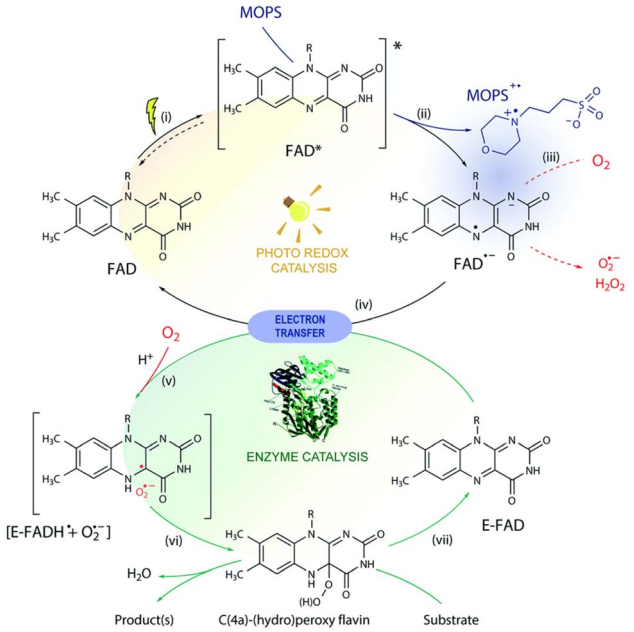
acid (MOPS), encourage photoinduced flavoenzyme-catalyzed asymmetric redox transformations by regenerating the flavin cofactor through sacrificial electron donation and by raising the functional stability of flavin-dependent oxidoreductase. In order to solve the oxygen problem in aerobic conditions, which is harmful to delicate enzymes, the active forms of flavin are stabilised by MOPS by creating a spin correlated ion pair ensemble, 3[flavin-MOPS$^+$] (Scheme 5).

2.6. Photobiocatalytic artificial dehalogenase for cross-coupling reactions

A light-harvesting metallo-enzyme platform for organometallic cross-coupling reactions under moderate conditions has been created by Wang *et al.*[81] It is feasible to increase the synergism of dual catalysis by rationally combining an artificial photosensitizer (*i.e.*, benzophenone) and a Ni^{II}(bpy) complex, two catalytic entities that are relatively incompatible in solution. The effective transformations of various aryl halides to phenols and a useful C–N bond formation were two examples of the catalytic utility. The use of the Ni^{II} cofactor, a wholly synthetic metal complex, also differs significantly from the most popular photobiocatalytic procedures that rely on natural redox enzymes. In addition, this synthetic enzyme is the first dehalogenase used for organic synthesis, which complements natural counterparts that are only known for bioremediation. As a result, this current study opens up new possibilities for combining synthetic photo and biocatalysts to push the limits of artificial enzyme catalysis for a variety of difficult bond configurations (Schemes 6 and 7).

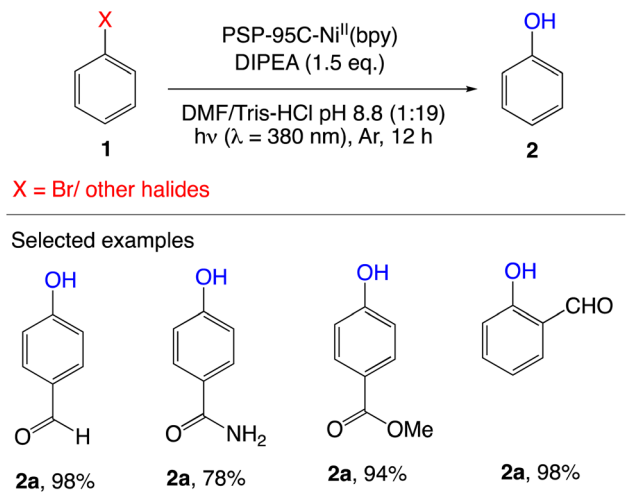
2.7. Aerobic photobiocatalysis

Due to the variety of enzymes available, their high catalytic activities and specificities, and the environmental friendliness



Scheme 5 Mechanism that has been proposed for MOPS-mediated photobiocatalysis. Steps of the photoredox cycle: (i) the oxidized FAD is excited by light to FAD*, capable of (ii) oxidizing MOPS. The resulting FAD semiquinone ($FAD^{\bullet-}$) can (iii) generate ROS in the presence of O_2 *via* electron transfer or (iv) reduce the oxidized FAD bound to the enzyme (E-FAD), regenerating its oxidized form FAD. Steps of the biocatalytic cycle: (v) the resulting caged radical pair [E-$FADH^{\bullet}$ + $O_2^{\bullet-}$] forms (vi) C(4a)-(hydro)peroxyflavin, responsible for the conversion of the substrate, and E-FAD is regenerated (vii). The ROS produced may induce enzyme deactivation, which is minimized in the presence of MOPS due to stabilization of the FAD semiquinone *via* formation of a [$FAD^{\bullet-}$–$MOPS^{\bullet+}$] ensemble (in purple). For simplicity, protonation equilibria are not shown. Reproduced with permission from ref. 80. Copyright © 2019 Royal Society of Chemistry.

of the processes, biocatalytic transformation has gained increasing attention in the field of green chemical synthesis. The majority of redox enzymes in nature rely on nicotinamide cofactors such as NAD^+/reduced NAD^+/nicotinamide adenine dinucleotide (NADH). An exceptional possibility to create fully integrated green processes is provided by the utilisation of solar energy, particularly visible light, in the creation of cofactors through the coupling of photocatalysis and biocatalysis. However, the quick decomposition and inactivation of the enzymatic material caused by photogenerated reactive oxygen species (ROS) has made the use of photocatalysts and enzymes difficult. Li *et al.* developed[82] core–shell structured polymer micelles and vesicles with aggregation-induced emission (AIE) properties as visible-light mediated photocatalysts for extremely stable and recyclable photobiocatalysis under aerobic conditions. The photoactive hydrophobic core of the polymer micelles and the hydrophobic membrane of the polymer vesicles can effectively regenerate NAD^+ from NADH, while the hydrophilic surface layer of the polymer colloids protects the enzymatic material (glucose 1-dehydrogenase) from the attack of photogenerated ROS. The enzyme maintains its active state after at least 10 regeneration cycles, and the polymer micelles and vesicles continue to function as photocatalysts. These polymer colloids could potentially help to establish commercially viable photobiocatalytic systems (Scheme 8).



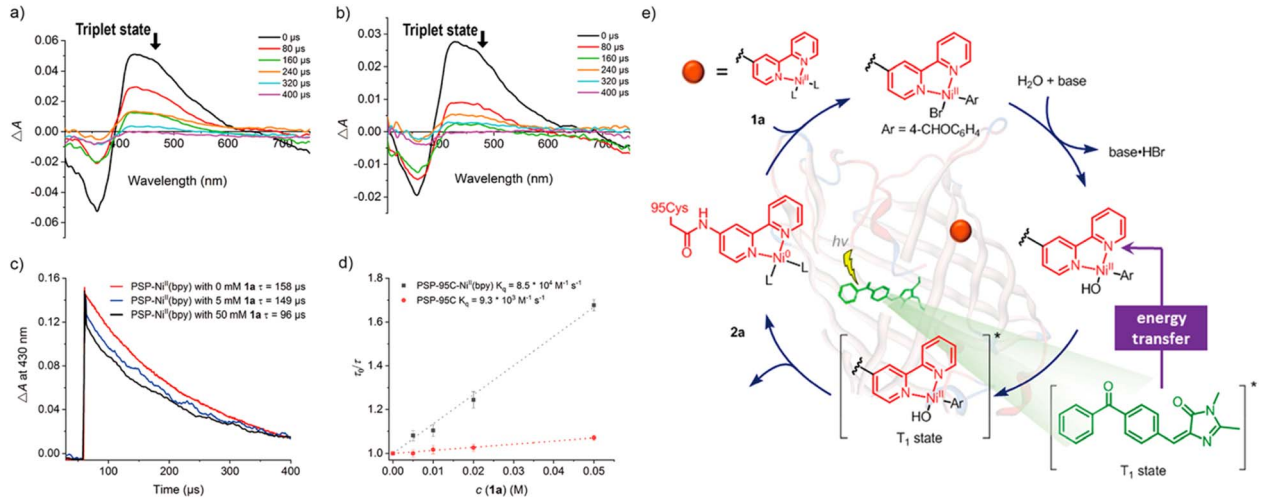
Scheme 6 Artificial dehalogenase for cross-coupling.[81]

2.8. Triplet–triplet annihilation-based photon-upconversion

The application of synthetic organic chemistry has been substantially expanded, particularly through the use of light-driven enzymatic catalysis. However, the restricted wavelength range of visible (sun)light can often only utilised by photoenzymes. Using triplet–triplet annihilation-based upconversion (TTA-UC), which transforms light with long wavelengths into light with shorter wavelengths, the wavelength range can be expanded. In their study on the viability of light upconversion, Park *et al.* developed[83] TTA-UC poly(styrene) (PS) nanoparticles that were doped with a platinum(II) octaethylporphyrin (PtOEP) photosensitizer and a 9,10-diphenylanthracene (DPA) annihilator (PtOEP:DPA@PS) Using 550 nm light, PtOEP:DPA@PS nanoparticles were photoexcited, resulting in the upconverted emission of DPA at 418 nm. With a high energy transfer efficiency, the TTA-UC emission may photoactivate flavin-dependent photodecarboxylases. As a result, under green light irradiation ($\lambda = 550$ nm), the photodecarboxylase from *Chlorella variabilis* NC64A was able to catalyse the conversion of fatty acids into long chain secondary alcohols (Scheme 9).

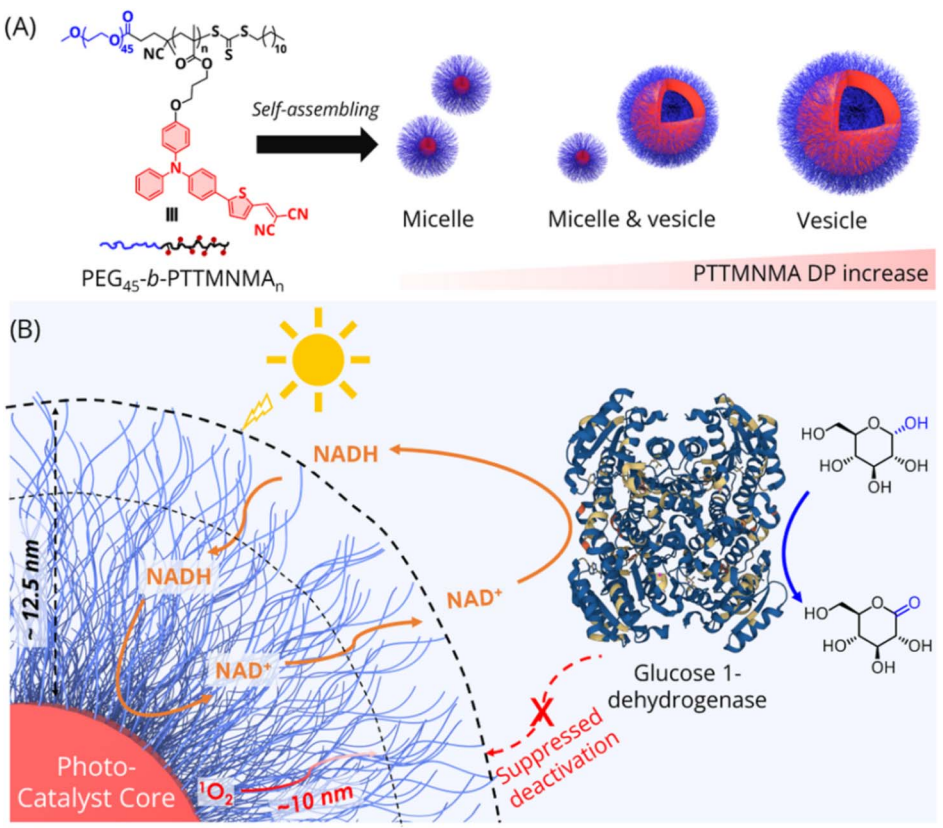
2.9. Photobiocatalytic synthesis of enantiopure 1-arylpropane-2-ols

Rodríguez-Fernández *et al.* have researched[84] how light-driven and biocatalyzed processes can work together. First, a photocatalytic Meerwein arylation was investigated to produce a series of 1-arylpropan-2-ones in aqueous solution using [Acr-Mes]ClO_4, an organic photosensitizer. Following the light-induced synthesis of the aryl radicals of the diazonium salt, an oxygenated radical intermediate was oxidised by the excited acridinium photocatalyst, followed by intramolecular electron transfer, producing the final products in a range of yields (15–95%). In order to reduce the ketone intermediates, stereo-

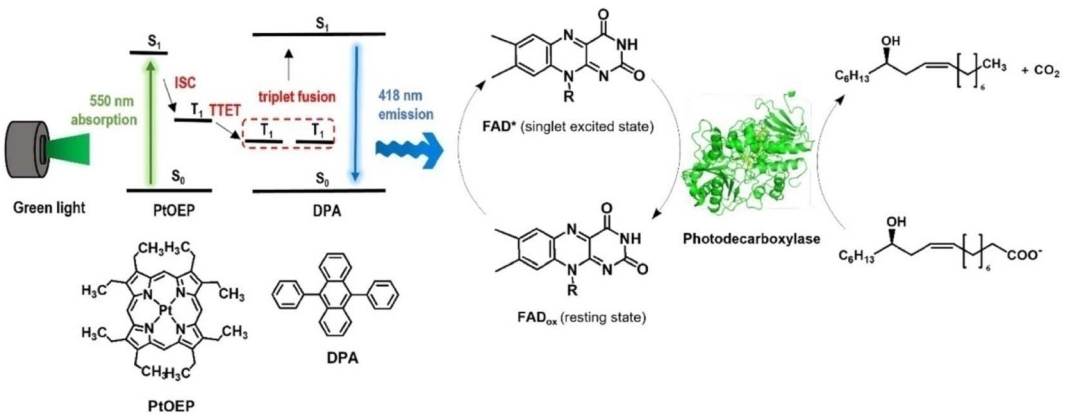


Scheme 7 Transient absorption studies and proposed plausible reaction mechanism. (a) PSP-95C-bpy in Tris–HCl pH 8.8 buffer. (b) PSP-95C-Ni^{II}(bpy) in Tris–HCl pH 8.8 buffer with bromide **1a** and DIPEA. (c) Kinetic traces of PSP-95C-Ni^{II}(bpy) with **1a** recorded at 430 nm in the presence of DIPEA. (d) Stern–Volmer plots and extracted quenching rate constants. (e) Plausible reaction mechanism. Reproduced with permission from ref. 81. Copyright © 2021 American Chemical Society.

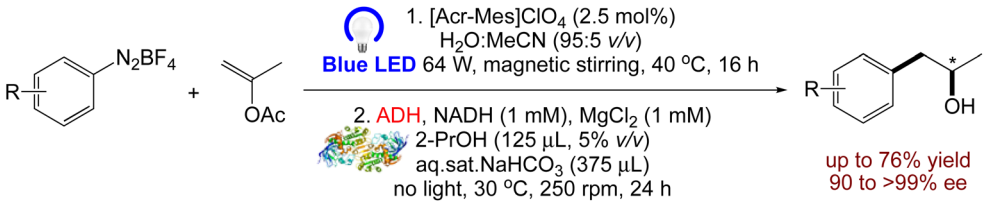
complementary alcohol dehydrogenases were used, taking advantage of the mild conditions used in this stage. Numerous valuable 1-arylpropan-2-ols were produced with low to good overall yields (14–76%) and excellent stereoselectivity (90 to >99% ee) *via* the screening various ADHs for the enzymatic carbonyl reduction and the optimisation of the reaction conditions to facilitate the sequential photobiocatalytic linear approach (Scheme 10).



Scheme 8 (A) The micelle and vesicle models of the chemical structure of the TTMN-based AIE block copolymers. (B) A demonstration of the aerobic photobiocatalysis system using glucose 1-dehydrogenase and a micelle/vesicle photocatalyst to carry out tandem photobiocatalytic reactions in aqueous solution. Reproduced with permission from ref. 82. Copyright © 2022 American Chemical Society.



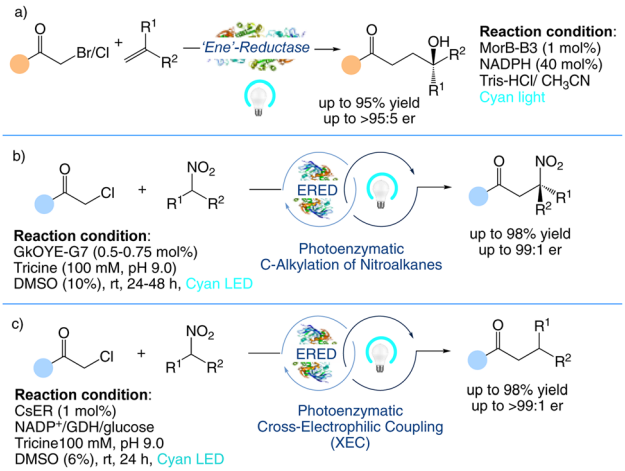
Scheme 9 Overall concept of triplet–triplet annihilation-based photon-upconversion (TTA-UC) for light-driven enzymatic catalysis. The TTA-UC allows the conversion of long wavelength light ($\lambda = 550$ nm) to short wavelength light ($\lambda = 418$ nm), which activates FAD in the enzymes for catalysis. PtOEP: platinum(II) octaethylporphyrin, DPA: 9,10-diphenylanthracene, ISC: intersystem crossing, TTET: triplet–triplet energy transfer. Reproduced with permission from ref. 83. Copyright © 2022, The Author(s).



Scheme 10 Synthesis of enantiopure 1-arylpropane-2-ols from aryl diazonium salts *via* a photobiocatalytic cascade.[84]

2.10. Photobiocatalytic asymmetric synthesis

Hyster *et al.* reported that flavin-dependent "*ene*"-reductases can catalyze the asymmetric synthesis of tertiary alcohols *via* a photoenzymatic alkene carbohydroxylation (Scheme 11a).[85] Mechanistic investigations indicate that the production of C–O bonds happens *via* a 5-*endo-trig* cyclization with the pendant ketone, resulting in an α-oxy radical that is subsequently hydrolyzed and oxidised to generate the product. Similarly, they also reported a highly chemo- and stereoselective *C*-alkylation of nitroalkanes with alkyl halides catalyzed by an engineered flavin-dependent "*ene*"-reductase (ERED) (Scheme 11b).[86] According to a mechanistic investigation, radical initiation is triggered by the excitation of an enzyme-templated charge–transfer complex that develops between the substrates and cofactor. Furthermore, they also reported a highly chemoselective and enantioselective Csp^3–Csp^3 photoenzymatic cross-electrophilic coupling (XEC) between alkyl halides and nitroalkanes catalysed by flavin-dependent '*ene*'-reductases (EREDs) (Scheme 11c).[87] This synthetic methodology demonstrates the unprecedented efficacy of biocatalysts in controlling stereoselectivity and differentiating Csp^3 electrophile substrates. In continuation of their work on asymmetric synthesis, the Hyster group have also carried out several other organic chemical transformations[88] using photobiocatalysis.



Scheme 11 Photobiocatalytic asymmetric synthesis. (a) Asymmetric carbohydroxylation of alkenes.[85] (b) Asymmetric *C*-alkylation of nitroalkanes.[86] (c) Asymmetric sp^3–sp^3 cross-electrophile coupling.[87]

3. Future prospects for photobiocatalysis

Since photobiocatalysis is still in its infancy, there are undoubtedly many obstacles as well as much potential in this emerging field. In this review, we have covered the most recent advances in the merging of photocatalysis with biocatalysis and its application in chemical transformations.[31] This field has developed several new opportunities with various challenges. In fact, the substance used as the photocatalyst plays a role in the conversion of light energy. The catalytic performance of the

cascade system will be further enhanced by using strong, superior photocatalysts and enzymes that are complementary to one another. It might be possible to accomplish difficult conversions with the combination of novel catalysts. The combination of controlled enzyme evolution and innovative biocatalytic reaction mechanisms holds enormous potential for addressing long-standing issues in chemical synthesis. The application of photobiocatalytic techniques will definitely enhance the range of chemical reactions that can be carried out by organic chemists. The use of photobiocatalysis will continue to be advanced further with new concepts and approaches.

4. Conclusions

In recent years, photobiocatalysis has grown at an exponential rate, revealing important variations in the biological processes involved, the most important of which is the way light drives the chemical transformation. Synthetic organic chemists have a growing awareness of the potential of photocatalysis and its application in synthetic problem-solving and are becoming more well-versed than ever. The potential to synthesise fine compounds in this rapidly developing area has been demonstrated by the tactics that have emerged in the last decade to combine photocatalysis with biocatalysis in an advantageous manner. Without the need for harsh chemicals or heat energy, visible light photoexcitation of naturally existing photoactive enzymatic cofactors might facilitate challenging reactions that are not achievable using ground-state catalysis. Although photocatalysis can facilitate a wider range of chemical transformations, biocatalysis benefits from the high selectivity that photochemistry at enzyme active sites provides, something made possible by the defined environment of the biocatalyst. However, for photobiocatalysis to be widely used, there must be defined guidelines for reporting photobiocatalytic experiments and access to reasonably priced, well-characterized illumination equipment. It is anticipated that light-dependent enzymatic reactions will become a common tool in biocatalytic laboratories as a result of all these discoveries.

Conflicts of interest

There are no conflicts to declare.

References

1 T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem.*, 2010, **2**, 527–532.
2 G. Ciamician, *Science*, 1912, **36**(926), 385–394.
3 A. Albini and M. Fagnoni, *Green Chem.*, 2004, **6**, 1–6.
4 L. Candish, K. D. Collins, G. C. Cook, J. J. Douglas, A. Gómez-Suárez, A. Jolit and S. Keess, *Chem. Rev.*, 2022, **122**, 2907–2980.
5 Z. C. Litman, Y. Wang, H. Zhao and J. F. Hartwig, *Nature*, 2018, **560**, 355–359.
6 Y. Wang, X. Huang, J. Hui, L. T. Vo and H. Zhao, *ACS Catal.*, 2020, **10**, 9431–9437.
7 X. Huang, B. Wang, Y. Wang, G. Jiang, J. Feng and H. Zhao, *Nature*, 2020, **584**, 69–74.
8 X. Huang, J. Feng, J. Cui, G. Jiang, W. Harrison, X. Zang, J. Zhou, B. Wang and H. Zhao, *Nat. Catal.*, 2022, **5**, 586–593.
9 N. Yang, Y. Tian, M. Zhang, X. Peng, F. Li, J. Li, Y. Li, B. Fan, F. Wang and H. Song, *Biotechnol. Adv.*, 2022, **54**, 107808.
10 Y. Tan, J. Ma, F. Zhang, S. Wang, F. Lan, H. Liu and R. Li, *ACS Sustainable Chem. Eng.*, 2022, **10**, 12065–12071.
11 S. Wu, R. Snajdrova, J. C. Moore, K. Baldenius and U. T. Bornscheuer, *Angew. Chem., Int. Ed.*, 2021, **60**, 88–119.
12 L. Hilterhaus, A. Liese, U. Kettling and G. Antranikian, *Applied Biocatalysis: From Fundamental Science to Industrial Applications*, Wiley-VCH, Weinheim, 2016.
13 J. M. Choi, S. S. Han and H. S. Kim, *Biotechnol. Adv.*, 2015, **33**, 1443–1454.
14 R. A. Sheldon and J. M. Woodley, *Chem. Rev.*, 2018, **118**, 801–838.
15 C. R. J. Stephenson, T. P. Yoon and D. W. C. MacMillan, *Visible Light Photocatalysis in Organic Chemistry*, Wiley-VCH, Weinheim, 2017.
16 M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926.
17 N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166.
18 J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102–113.
19 L. Marzo, S. K. Pagire, O. Reiser and B. König, *Angew. Chem., Int. Ed.*, 2018, **57**, 10034–10072.
20 C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363.
21 F. Strieth-Kalthoff and F. Glorius, *Chem*, 2020, **6**, 1888–1903.
22 V. Alphand, J. H. V. B. Willem, V. Jurkaš, S. Kara, R. Kourist, W. Kroutil, F. Mascia, M. F. Nowaczyk, C. E. Paul, S. Schmidt, J. Spasic, P. Tamagnini and C. K. Winkler, *ChemPhotoChem*, 2023, **7**, e202200325.
23 L. Schmermund, V. Jurkas, F. F. Özgen, G. D. Barone, H. C. Büchsenschütz, C. K. Winkler, S. Schmidt, R. Kourist and W. Kroutil, *ACS Catal.*, 2019, **9**, 4115–4144.
24 R. Amanaka and K. Nakamura, Photobiocatalysis, in *Future Directions in Biocatalysis*, ed. T. Matsuda, Elsevier, Amsterdam, 2017.
25 S. Zhang, S. Liu, Y. Sun, S. Li, J. Shi and Z. Jiang, *Chem. Soc. Rev.*, 2021, **50**, 13449–13466.
26 W. Harrison, X. Huang and H. Zhao, *Acc. Chem. Res.*, 2022, **55**, 1087–1096.
27 K. Chen and F. H. Arnold, *Nat. Catal.*, 2020, **3**, 203–213.
28 C. K. Prier and F. H. Arnold, *J. Am. Chem. Soc.*, 2015, **137**, 13992–14006.
29 E. Meggers, *Chem. Commun.*, 2015, **51**, 3290–3301.
30 B. T. Nicholls, D. G. Oblinsky, S. I. Kurtoic, D. Grosheva, Y. Ye, G. D. Scholes and T. K. Hyster, *Angew. Chem., Int. Ed.*, 2022, **61**, e202113842.
31 Y. Peng, Z. Chen, J. Xu and Q. Wu, *Org. Process Res. Dev.*, 2022, **26**, 1900–1913.
32 J. S. Catharina and T. Gulder, *ChemBioChem*, 2019, **20**, 1871–1897.

33 S. H. Lee, D. S. Choi, S. K. Kuk and C. B. Park, *Angew. Chem., Int. Ed.*, 2018, **57**, 7958–7985.
34 M. A. Emmanuel, S. G. Bender, C. Bilodeau, J. M. Carceller, J. S. DeHovitz, H. Fu, Y. Liu, B. T. Nicholls, Y. Ouyang, C. G. Page, T. Qiao, F. C. Raps, D. R. Sorigué, S.-Z. Sun, J. Turek-Herman, Y. Ye, A. Rivas-Souchet, J. Cao and T. K. Hyster, *Chem. Rev.*, 2023, **123**(9), 5459–5520.
35 J. A. Maciμ-Agulló, A. Corma and H. Garcia, *Chem.–Eur. J.*, 2015, **21**, 10940–10959.
36 (*a*) N. Kosem, M. Watanabe, J. T. Song, A. Takagaki and T. Ishihara, *Appl. Catal., A*, 2023, **651**, 119019; (*b*) S. Shi, C. Zeng, T. Si, B. Wang and P. K. Wong, *ACS ES&T Engg*, 2022, **2**(6), 989–1000.
37 C.-H. Yun, J. Kim, F. Hollmann and C. B. Park, *Chem. Sci.*, 2022, **13**, 12260.
38 (*a*) V. Srivastava, P. K. Singh and P. P. Singh, *Croat. Chem. Acta*, 2014, **87**, 91–95; (*b*) V. Srivastava, P. K. Singh and P. P. Singh, *Chem. Heterocycl. Compd.*, 2014, **50**, 573–578; (*c*) V. Srivastava, P. K. Singh and P. P. Singh, *Croat. Chem. Acta*, 2015, **88**, 59–65; (*d*) V. Srivastava, P. K. Singh and P. P. Singh, *Croat. Chem. Acta*, 2015, **88**, 227–233; (*e*) V. Srivastava, P. K. Singh and P. P. Singh, *Asian J. Chem.*, 2016, **28**, 2159–2163; (*f*) V. Srivastava, P. K. Singh and P. P. Singh, *Rev. Roum. Chim.*, 2016, **61**, 755–761; (*g*) V. Srivastava, P. K. Singh and P. P. Singh, *Croat. Chem. Acta*, 2017, **90**, 435–441; (*h*) V. Srivastava, P. K. Singh, S. Kanaujia and P. P. Singh, *New J. Chem.*, 2018, **42**, 688–691; (*i*) P. K. Singh, P. P. Singh and V. Srivastava, *Croat. Chem. Acta*, 2018, **91**, 383–387; (*j*) V. Srivastava, P. K. Singh and P. P. Singh, *Tetrahedron Lett.*, 2019, **60**, 40–43; (*k*) V. Srivastava, P. K. Singh and P. P. Singh, *Tetrahedron Lett.*, 2019, **60**, 1333–1336; (*l*) V. Srivastava, P. K. Singh and P. P. Singh, *Tetrahedron Lett.*, 2019, **60**, 151041; (*m*) P. P. Singh and V. Srivastava, *ChemistrySelect*, 2023, **8**(44), e202302732.
39 (*a*) V. Srivastava, P. K. Singh, A. Srivastava and P. P. Singh, *RSC Adv.*, 2020, **10**, 20046–20056; (*b*) V. Srivastava, P. K. Singh and P. P. Singh, *Rev. Roum. Chim.*, 2020, **65**, 221–226; (*c*) A. Srivastava, P. K. Singh, A. Ali, P. P. Singh and V. Srivastava, *RSC Adv.*, 2020, **10**, 39495–39508; (*d*) V. Srivastava, P. K. Singh, A. Srivastava and P. P. Singh, *RSC Adv.*, 2021, **11**, 14251–14259; (*e*) V. Srivastava and P. P. Singh, *Org. Biomol. Chem.*, 2021, **19**, 313–321; (*f*) P. P. Singh, P. K. Singh, M. Z. Beg, A. Kashyap and V. Srivastava, *Synth. Commun.*, 2021, **51**, 3033–3058; (*g*) V. Srivastava, P. K. Singh, A. Srivastava, S. Sinha and P. P. Singh, *Photochemistry*, 2021, **1**, 237–276; (*h*) V. Srivastava, P. K. Singh, S. Tivari and P. P. Singh, *Org. Chem. Front.*, 2022, **9**, 1485–1507; (*i*) V. Srivastava, P. K. Singh and P. P. Singh, *J. Photochem. Photobiol., C*, 2022, **50**, 100488; (*j*) P. P. Singh and V. Srivastava, *RSC Adv.*, 2022, **12**, 18245–18265; (*k*) P. P. Singh, G. Pandey, S. Sinha and V. Srivastava, *RSC Adv.*, 2022, **12**, 29826; (*l*) S. Tivari, P. K. Singh, P. P. Singh and V. Srivastava, *RSC Adv.*, 2022, **12**, 35221; (*m*) M. Mishra, V. Srivastava, P. K. Singh and P. P. Singh, *Croat. Chem. Acta*, 2022, **95**, 25–30; (*n*) S. P. Singh, V. Srivastava, P. K. Singh and P. P. Singh, *Tetrahedron*, 2023, **132**, 133245; (*o*) M. Z. Beg, P. K. Singh, P. P. Singh, M. Srivastava and V. Srivastava, *Mol. Diversity*, 2023, DOI: 10.1007/s11030-022-10595-2; (*p*) V. Srivastava, S. Tivari, P. K. Singh and P. P. Singh, *Catal. Lett.*, 2023, DOI: 10.1007/s10562-023-04345-8; (*q*) P. P. Singh, P. K. Singh and V. Srivastava, *Org. Chem. Front.*, 2023, **10**, 216–236; (*r*) P. P. Singh, J. Singh and V. Srivastava, *RSC Adv.*, 2023, **13**, 10958–10986; (*s*) V. P. Singh, A. K. Singh, V. Srivastava and P. P. Singh, *Tetrahedron*, 2023, **147**, 133658.
40 S. Shi, C. Zeng, T. Si, B. Wang and P. K. Wong, *ACS ES&T Engg*, 2022, **2**, 989–1000.
41 N. Kosem, M. Watanabe, J. T. Songa, A. Takagakia and T. Ishihara, *Appl. Catal., A*, 2023, **651**, 119019.
42 Y. Ding, J. R. Bertram, C. Eckert, R. R. Bommareddy, R. Patel, A. Conradie, S. Bryan and P. Nagpal, *J. Am. Chem. Soc.*, 2019, **141**(26), 10272–10282.
43 M. Martins, C. Toste and I. A. C. Pereira, *Angew. Chem., Int. Ed.*, 2021, **60**(16), 9055–9062.
44 Y. Honda, H. Hagiwara, S. Ida and T. Ishihara, *Angew. Chem.*, 2016, **128**(28), 8177–8180.
45 B. Wang, C. Zeng, K. H. Chu, D. Wu, H. Y. Yip, L. Ye and P. K. Wong, *Adv. Energy Mater.*, 2017, **7**(20), 1700611.
46 Z. Jiang, B. Wang, J. C. Yu, J. Wang, T. An, H. Zhao, H. Li, S. Yuan and P. K. Wong, *Nano Energy*, 2018, **46**, 234–240.
47 W. Wei, P. Sun, Z. Li, K. Song, W. Su, B. Wang, Y. Liu and J. Zhao, *Sci. Adv.*, 2018, **4**(2), eaap9253.
48 B. Ramprakash and A. Incharoensakdi, *Bioresour. Technol.*, 2020, **318**, 124057.
49 Y. Honda, Y. Shinohara and H. Fujii, *Catal. Sci. Technol.*, 2020, **10**(17), 6006–6012.
50 K. Xiao, T. H. Tsang, D. Sun, J. Liang, H. Zhao, Z. Jiang, B. Wang, J. C. Yu and P. K. Wong, *Adv. Energy Mater.*, 2021, **11**(21), 2100291.
51 H. S. Chan, K. Xiao, T. H. Tsang, C. Zeng, B. Wang, X. Peng and P. K. Wong, *Front. Microbiol.*, 2021, **12**, 654033.
52 B. Wang, K. Xiao, Z. Jiang, J. Wang, J. C. Yu and P. K. Wong, *Energy Environ. Sci.*, 2019, **12**(7), 2185–2191.
53 Z. Wang, D. Gao, H. Geng and C. Xing, *J. Mater. Chem. A*, 2021, **9**(35), 19788–19795.
54 S. F. Rowe, G. L. Gall, E. V. Ainsworth, J. A. Davies, C. W. J. Lockwood, L. Shi, A. Elliston, I. N. Roberts, K. W. Waldron, D. J. Richardson, T. A. Clarke, L. J. C. Jeuken, E. Reisner and J. N. Butt, *ACS Catal.*, 2017, **7**(11), 7558–7566.
55 H. Shen, Y. Z. Wang, G. Liu, L. Li, R. Xia, B. Luo, J. Wang, D. Suo, W. Shi and Y. C. Yong, *ACS Catal.*, 2020, **10**(22), 13290–13295.
56 B. Luo, Y. Z. Wang, D. Li, H. Shen, L. X. Xu, Z. Fang, Z. Xia, J. Ren, W. Shi and Y. C. Yong, *Adv. Energy Mater.*, 2021, **11**(19), 2100256.
57 C. Du, X. Wang, W. Chen, S. Feng, J. Wen and Y. Wu, *Mater. Today Adv.*, 2020, **6**, 100071.
58 H. Xie, J. Wang, K. Ithisuphalap, G. Wu and Q. Li, *J. Energy Chem.*, 2017, **26**(6), 1039–1049.
59 F. Li, Y. C. Li, Z. Wang, J. Li, D. H. Nam, Y. Lum, M. Luo, X. Wang, A. Ozden, S. F. Hung, B. Chen, Y. Wang, J. Wicks,

Y. Xu, Y. Li, C. M. Gabardo, C. T. Dinh, Y. Wang, T. T. Zhuang, D. Sinton and E. H. Sargent, *Nat. Catal.*, 2020, **3**(1), 75–82.
60 X. Wang, C. Gao, J. Low, K. Mao, D. Duan, S. Chen, R. Ye, Y. Qiu, J. Ma, X. Zheng, R. Long, X. Wu, L. Song, J. Zhu and Y. Xiong, *Sci. Bull.*, 2021, **66**(13), 1296–1304.
61 M. B. Ross, P. D. Luna, Y. Li, C. T. Dinh, D. Kim, P. Yang and E. H. Sargent, *Nat. Catal.*, 2019, **2**(8), 648–658.
62 H. Salehizadeh, N. Yan and R. Farnood, *Chem. Eng. J.*, 2020, **390**(15), 124584.
63 C. Rudolf and H. Grammel, *Enzyme Microb. Technol.*, 2012, **50**(4–5), 238–246.
64 Y. Wang, J. Liu, Y. Wang, A. M. Al-Enizi and G. Zheng, *Small*, 2017, **13**(43), 1701809.
65 K. C. Christoforidis and P. Fornasiero, *ChemCatChem*, 2019, **11**(1), 368–382.
66 (*a*) Q. Wang, J. Warnan, S. Rodríguez-Jiménez, J. J. Leung, S. Kalathil, V. Andrei, K. Domen and E. Reisner, *Nat. Energy*, 2020, **5**(9), 703–710; (*b*) Y. Wang, E. Chen and J. Tang, *ACS Catal.*, 2022, **12**, 7300–7316.
67 G. Hu, Z. Li, D. Ma, C. Ye, L. Zhang, C. Gao, L. Liu and X. Chen, *Nat. Catal.*, 2021, **4**(5), 395–406.
68 J. Ye, J. Yu, Y. Zhang, M. Chen, X. Liu, S. Zhou and Z. He, *Appl. Catal., B*, 2019, **257**(15), 117916.
69 J. Ye, G. Ren, L. Kang, Y. Zhang, X. Liu, S. Zhou and Z. He, *iScience*, 2020, **23**(7), 101287.
70 P. Gai, W. Yu, H. Zhao, R. Qi, F. Li, L. Liu, F. Lv and S. Wang, *Angew. Chem., Int. Ed.*, 2020, **59**(18), 7224–7229.
71 K. K. Sakimoto, A. B. Wong and P. Yang, *Science*, 2016, **351**(6268), 74–77.
72 K. K. Sakimoto, S. J. Zhang and P. Yang, *Nano Lett.*, 2016, **16**(9), 5883–5887.
73 H. Zhang, H. Liu, Z. Tian, D. Lu and Y. Yu, *Nat. Nanotechnol.*, 2018, **13**(10), 900–905.
74 S. Cestellos-Blanco, H. Zhang and P. Yang, *Faraday Discuss.*, 2019, **215**, 54–65.
75 M. Y. Chen, Z. Fang, L. X. Xu, D. Zhou, X. J. Yang, H. J. Zhu and Y. C. Yong, *Bioresour. Bioprocess.*, 2021, **8**, 30.
76 B. Wang, Z. Jiang, J. C. Yu, J. Wang and P. K. Wong, *Nanoscale*, 2019, **11**(19), 9296–9301.
77 Y. Su, S. Cestellos-Blanco, J. M. Kim, Y.-x. Shen, Q. Kong, D. Lu, C. Liu, H. Zhang, Y. Cao and P. Yang, *Joule*, 2020, **4**(4), 800–811.
78 S. Zhang, Y. Zhang, Y. Chen, D. Yang, S. Li, Y. Wu, Y. Sun, Y. Cheng, J. Shi and Z. Jiang, *ACS Catal.*, 2021, **11**, 476–483.
79 A. K. Mengele, D. Weixler, S. Amthor, B. J. Eikmanns, G. M. Seibold and S. Rau, *Angew. Chem., Int. Ed.*, 2022, **61**, e202114842.
80 L. C. P. Gonçalves, H. R. Mansouri, E. L. Bastos, M. Abdellah, B. S. Fadiga, J. S. Rudroff and M. D. Mihovilovic, *Catal. Sci. Technol.*, 2019, **9**, 1365.
81 Y. Fu, J. Huang, Y. Wu, X. Liu, F. Zhong and J. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 617–622.
82 N. Zhang, S. Trépout, H. Chen and M.-H. Li, *J. Am. Chem. Soc.*, 2023, **145**, 288–299.
83 S. -Y. Hwang, D. Song, E. -J. Seo, F. Hollmann, Y. You and J. -B. Park, *Sci. Rep.*, 2022, **12**, 9397.
84 L. Rodríguez-Fernández, J. Albarrán-Velo, I. Lavandera and V. Gotor-Fernández, *Adv. Synth. Catal.*, 2023, **365**, 1883–1892.
85 Y. Ouyang, J. Turek-Herman, T. Qiao and T. K. Hyster, *J. Am. Chem. Soc.*, 2023, **145**, 17018–17022.
86 C. G. Page, J. Cao, D. G. Oblinsky, S. N. MacMillan, S. Dahagam, R. M. Lloyd, S. J. Charnock, G. D. Scholes and T. K. Hyster, *J. Am. Chem. Soc.*, 2023, **145**, 11866–11874.
87 H. Fu, J. Cao, T. Qiao, Y. Qi, S. J. Charnock, S. Garfinkle and T. K. Hyster, *Nature*, 2022, **610**, 302–307.
88 (*a*) S. G. Bender and T. K. Hyster, *ACS Catal.*, 2023, **13**, 14680–14684; (*b*) H. D. Clements, A. R. Flynn, B. T. Nicholls, D. Grosheva, S. J. Lefave, M. T. Merriman, T. K. Hyster and M. S. Sigman, *J. Am. Chem. Soc.*, 2023, **145**(32), 17656–17664; (*c*) Y. Ye, J. Cao, D. G. Oblinsky, D. Verma, C. K. Prier, G. D. Scholes and T. K. Hyster, *Nat. Chem.*, 2023, **15**, 206–212.