

**Solar Fuels and Feedstocks: The Quest for Renewable Black Gold**

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Photocatalysis for organic synthesis is a tool capable of C–C, C–O and C–N bond transformations. This technology has the potential to transform the chemical manufacturing industry and support growing demand for chemical feedstocks. Compared to traditional catalysis, photocatalysis can access alternative reaction pathways that lower the overall energy requirement and operate at or near ambient conditions. A key challenge is the delivery of photoenergy at the scale required for rapid and efficient operation of the catalyst. The development of efficient, broad-spectrum light harvesting devices that funnel light energy to a catalyst, along with catalyst design to selectively enable high-energy reactions, are necessary steps towards solar fuels and feedstocks. This perspective highlights some recent advances in photocatalysis and advocates for expanding the scope of photocatalysis for large-scale industrial applications.

Introduction

Every aspect of modern society is dependent on chemical manufacturing. The ubiquity of chemical products, from the dye in our clothing to the packaging for our food and medical supplies, makes it easy to overlook their energy costs. Chemical manufacturing accounts for 25% of the global GDP and the bulk of feedstock chemicals and fuels are extracted from oil, gas and coal.^{1,2} The use of fossil fuels is increasing at a greater rate for chemical manufacturing than for any other industry, and is expected to exceed transportation demands by 2050.³

Energy-intensive processes are required to generate the molecular components of modern society; nearly equal amounts of fossil fuels are consumed to generate the high temperatures and pressures needed for synthetic reactions as are transformed into the end products.²⁻⁴ Reducing the dependency on fossil fuels as both fuel and raw material in generating everyday chemicals is therefore an important goal for reducing the environmental impact of the entire industry. Indeed, production of feedstock chemicals and fuels from biomass with minimized environmental impact has been a long-time aim, but technology has not yet emerged to make alternative fuels and feedstocks competitive with petrochemicals.²⁻⁶

All fossil fuels originate from biomass, which was converted to coal, oil, and natural gas over millions of years of geological processing.⁷ Catalytic systems that break down biomass and convert small molecules to feedstock chemicals and fuels could

bypass the long-term carbon cycle and expand the scope of renewable resources. Although ethanol is currently produced from biomass on an industrial scale, competition for agricultural resources to produce either food or fuel can lead to food insecurity.⁸ Lignocellulose is an appealing source for aromatic feedstocks and can be obtained from waste, but requires further development for industrial application.⁹⁻¹²

Solar energy is arguably the most important renewable energy resource available to humanity.¹³ The annual insolation received within the United States based on Global Horizontal Irradiation varies between 1200 and 2200 kWh/m².¹⁴ Chemical manufacturing in the United States consumed 2858 trillion BTU (8.4×10^{11} kWh) for fuel and power in 2018.¹ Direct solar energy conversion at 100% efficiency would require an area of 700 km², approximately the size of Singapore, to meet the annual chemical manufacturing energy demand.

Solar manufacturing, the application of solar-powered photochemistry to the industrial synthesis of chemicals, has the potential to support the growing demand for chemical products by lowering the process energy requirements, provide synthetically feasible approaches to obtain feedstocks from alternative sources, and transform the process energy input from heat and pressure to light. Photocatalysis frequently accesses alternative reaction pathways with improved selectivity and yields compared to traditional catalysts.¹⁵ Although industrial standards vary by region and chemical product, energy-saving technology is in demand across the manufacturing sector.^{3, 16} This Perspective highlights the advances made in photocatalysis to address the issues of both energy-intensive reaction conditions and the limited availability of synthetic routes to high-volume products that use non-petrochemical feedstocks.

Figure 1 shows the photon flux vs. photon energy of the ASTM G-173 solar spectrum.¹⁷ While several spectral dips arise from

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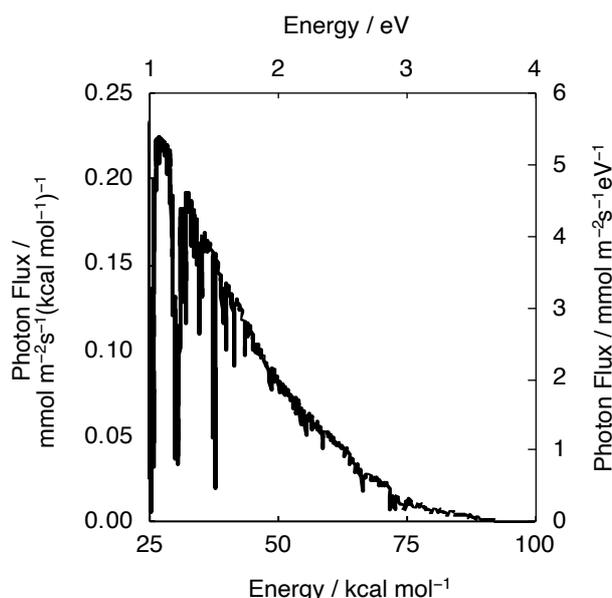


Fig. 1. Photon flux vs. photon energy of the ASTM G-173 solar spectrum.¹⁷

the absorption of water vapor, O₂, O₃, and CO₂ in the atmosphere, the overall increase of photon flux is monotonic as photon energy decreases from 4 to 1 eV (100 to 25 kcal mol⁻¹). Solar irradiation possesses sufficient energy to break many of the molecular bonds on Earth, but high activation energies prevent decomposition and preserve our existence. The photons in the red and near infrared regions are abundant but provide insufficient energy to drive reactions that are thermodynamically uphill – that is, where the products are *less* stable than the reactants – by more than about 50 kcal mol⁻¹ or 2 eV. Inspired by the way in which photosynthesis combines the energy of multiple photons to actuate redox states, multiphoton processes can enable chemical reactions that are otherwise prohibitively disfavored at equilibrium.

The term “photocatalysis” is broadly applied to systems that capture energy from light and use that energy to drive reactions. Light-capture techniques include molecular photosensitizers, solar panel materials, quantum dots, and dye-sensitized solar cells. The ideal light-capturing system efficiently absorbs light over a broad spectrum and funnels energy or electrons to a catalyst.¹⁸ The relevant excited state of a molecular photosensitizer must be thermodynamically capable of either energy or electron transfer and must be sufficiently long-lived to engage in such reactions: at least in the nanosecond time regime for diffusion-limited processes.^{19, 20} The roles of light absorption and catalysis might be performed by a single species, the *photocatalyst*, or two separate moieties, the *photosensitizer* and the *catalyst*.^{21–25}

Inspired by photosynthesis, photocatalysis was originally developed for water splitting and CO₂ reduction, two thermodynamically uphill reactions.^{26–31} Early photocatalytic systems employed a molecular photosensitizer, typically [Ru(bpy)₃]²⁺, to undergo photoinitiated electron transfer to a proton reduction catalyst.^{26, 27, 32, 33} Around the same time, the

first reports of [Ru(bpy)₃]²⁺ used as a photocatalyst in organic synthesis appeared.^{34–36} Photocatalyzed activation of a C–H bond was first observed as unintentional carbonylation of benzene solvent.³⁷ Advances in molecular photocatalysis include the ability to activate catalysts via energy transfer,^{38–40} access strongly reducing potentials,^{23, 41–43} and incorporate proton-coupled electron transfer.^{44, 45}

Solar Manufacturing

Photocatalysis provides a means to conduct reactions that typically require harsh conditions under ambient pressure and at room temperature, often with improved selectivity for specific products. The reaction scope of photocatalysis has expanded immensely since it was first employed in organic synthesis and now includes C–C and C–heteroatom (O, N, and halogens, among others) bond forming reactions.^{15, 46–48} Photocatalysis is already routinely applied to pharmaceutical manufacturing,⁴⁹ and in principle can be extended to other chemical products to meet the needs of the chemical manufacturing industry. The development of solar manufacturing for a broad range of chemicals would have a tremendous impact on energy resources and the environment. The reaction scale and environmental impact of industrial N₂ fixation, polymer synthesis, and agrochemicals far exceed pharmaceutical manufacturing and require low-cost manufacturing technology (Fig. 2).² The primary challenges for the actualization of solar manufacturing are 1) the development of efficient and stable light harvesters and photocatalysts for high energy bond activation and 2) the design and implementation of photochemical reactors for high-volume chemical production. Industrial scale photoredox chemistry is dominated by homogenous molecular catalysts including iridium and ruthenium based transition metal complexes, echoing trends in laboratory scale usage over the last decade.^{15, 50–53} Molecular photocatalysts are more efficient than heterogenous catalysts in terms of both photon and mass transport.⁵⁴ Nonetheless, photocatalysis strategies suffer from the costs associated with precious metal-based catalysts and limited scalability due to the need for illumination in reaction vessels.^{55–57} Recent work has demonstrated the use of non-metallic catalysts with efficiencies comparable to the commonly used iridium and ruthenium catalysts, thus offering more cost-effective synthesis routes.^{58, 59} Development of photocatalysts with visible-range absorption as well as larger absorption cross-sections has assisted the efficiency of reactions under illumination constraints, paving the way for greater reaction scalability.^{60–62} Flow chemistry based reactor design also has the potential to improve reaction efficiency through enhanced illumination of the homogenous catalyst.^{56, 63, 64}

The energy of light harnessed by photocatalytic systems can overcome prohibitive activation energies, drive thermodynamically uphill reactions,⁶⁵ and selectively catalyze one of many reaction pathways.⁶⁶ Enzymes selectively catalyze one reaction pathway by simultaneously lowering the activation energy for the desired product and increasing the energy barrier for other possible reaction paths, inhibiting side product

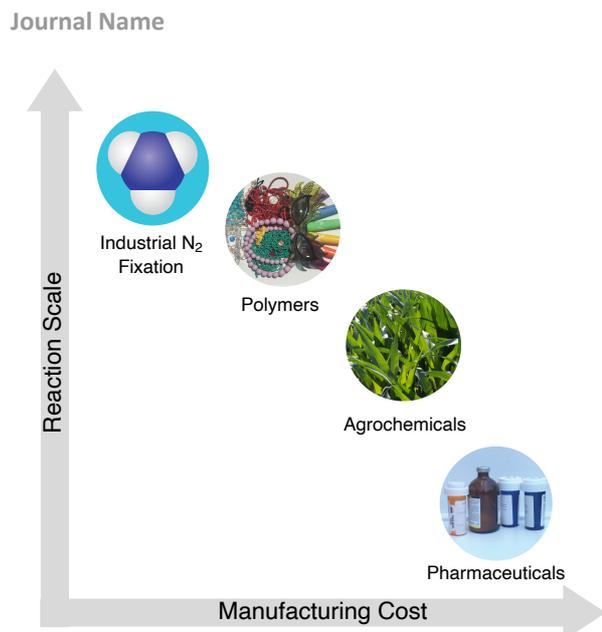


Fig. 2. Qualitative depiction of manufacturing scale and cost of chemicals for various applications. The top 70 energy-consuming chemical products, based on reaction scale and conditions, are provided by the U.S. Department of Energy.² Photocatalysis has been primarily employed in medicinal chemistry and artificial photosynthesis. Further innovation of solar manufacturing for agrochemicals, plastics and ammonia is necessary to meet the global demand.

formation.⁶⁷ Photocatalysis can also provide product selectivity by overcoming the activation energy for one reaction pathway and bypassing alternative product reactions. For example, the Meerwein reaction for olefin arylation, important for synthesis of stilbenes used as dyes,⁶⁸ was plagued by low product yields (20–40%) and formation of multiple side products for over 70 years.⁶⁹ Selective photocatalytic olefin arylation with yields up to 94% and no detectable byproducts was reported in 2012.⁶⁶ Ideal comparisons between conventional and photocatalysis and between multiple photocatalyzed reactions should include analysis of the quantum yields; that is, mole product per mole photon.^{70–72} Although quantum yields are frequently unreported in organic synthesis, we recommend quantum yield as the appropriate metric to benchmark photocatalyst efficiency.

The applications and mechanisms of photocatalysis are expansive. To elaborate the potential role of photocatalysis in decreasing the energy cost for chemical manufacturing, we here provide a few vignettes of the transformations that photocatalysis can accomplish, with a special focus on the reaction classes of potential industrial interest enabled by photocatalysis.

Non-Petrochemical Feedstocks

Polymer upcycling and depolymerization of lignin are alternative sources of feedstock chemicals that currently offer opportunities for further research development.^{73–75} Polymer upcycling, or chemical recycling, is the depolymerization of plastics into monomeric units. Polymer upcycling has a dual benefit of waste management and as an alternative source of

feedstock chemicals.^{76, 77} Currently, most polymer recycling produces low grade plastics and the growing demand for high quality polymers coincides with growing fossil fuel demand.³ Polymer upcycling is an essential step in producing high-quality recycled plastics. Polymers have been chemically recycled via heterogeneous catalysis,⁷⁸ but photocatalyzed polymer upcycling has not yet been reported. Photocatalyzed polymer upcycling would provide a method to store solar energy in the form of feedstock chemicals.

Lignin, the biopolymer that gives rigidity to plants, is a highly abundant agricultural waste product.^{75, 79, 80} Lignin depolymerization produces methoxy-substituted phenol monomers that can be utilized as bio-sourced feedstocks.¹¹ However, monomer arrangement in lignin is complex and the polymer structure varies from one plant species to another.^{81, 82} Reaction conditions requiring stoichiometric quantities of acid, polymer complexity, and difficulty separating multiple products have limited industrial adoption of lignin feedstock.¹⁰ Selective bond cleavage was recently demonstrated in photocatalyzed lignin depolymerization, enabling facile monomer extraction.⁸³

General Mechanism of Homogeneous and Heterogeneous Catalysis

Although detailed mechanistic pictures differ from reaction to reaction, they share certain common features or elementary steps. Here we focus on the one-photon initiated mechanisms that prevail in photocatalysis. Other strategies recently proposed based on the input of multiple photons⁸⁴ either simultaneously⁸⁵ or sequentially^{23, 86, 87} are beyond the scope of this article.

In general, homogenous photocatalysis starts with a light absorption event to generate an electronically excited chromophore that can engage in either electron/hole or energy transfer to a suitable acceptor. These processes lead to the formation of reactive species that can engage in elementary steps to form the desired products. Alternatively, the electron/hole or energy transfer may activate a secondary catalyst, which can either generate or trap transient radical species, thus directing the synthetic output.⁸⁸ In solution, these transfer steps are usually kinetically controlled by bimolecular diffusion between the chromophores and substrates, which sets a lower limit for the excited-state lifetime of the chromophore, which must persist in solution for at least several nanoseconds.⁸⁹

In heterogeneous photocatalysis, substrates are usually adsorbed onto the surface of the solid-state photocatalysts prior to light absorption. Subsequent photoexcitation leads to the formation of the electrons and holes in the photocatalysts, which can either recombine back to the ground state or diffuse to substrate-bound active sites. The diffusion of these charge carriers within the solid-state materials usually proceeds faster than diffusion in solution due to their smaller masses as well as less bath fluctuation in the consistently arranged crystal lattice. The oxidized/reduced substrates can undergo either elementary bond-forming/bond-breaking steps supported by

often used for heterogeneous photocatalysis. Recyclability and easy synthesis of the catalysts significantly reduce cost, an important factor for industrial-scale processes.⁹¹⁻⁹⁴ Several reactions, including dehydrogenation as well as partial and total oxidation, have been demonstrated. Industrial-scale water detoxification, gas pollutant removal, solar fuel production, etc. would benefit from heterogeneous photocatalysis, due to its low energy consumption.

Consideration of a free energy landscape that describes reaction intermediates and deactivation paths may be useful for the rational design of photocatalytic systems. Hydroamidation is an important reaction used in the production of several biologically active compounds.^{95, 96} Photocatalytic hydroamidation utilizes photoinitiated proton-coupled electron transfer (PCET) to enable the direct homolysis of a strong amide N—H bond, leading to productive C—N bond formation (Fig. 3).⁹⁷ Spectroscopic studies provide insight into the intricate mechanism of this reaction.⁹⁸ The free energy landscape for photocatalyzed hydroamidation in Fig. 3 qualitatively depicts free energy wells of reaction intermediates based on spectroscopically determined rate constants. In this reaction, three unproductive pathways compete with the forward reaction: excited state relaxation, charge recombination, and a hydrogen atom transfer (HAT) side reaction.

Minimizing the loss of photon energy to competitive unproductive paths is a current opportunity to improve quantum yield and shorten reaction times. Although the specific steps in which photon energy is lost can be unique to individual reaction mechanisms, excited state relaxation and charge recombination are common to all photoredox reactions. It is important to consider all deactivation pathways to improve photocatalyst efficiency.

C—C Bond Formation

The formation of C—C bonds is central to organic chemistry. The majority of the photocatalytic transformations to generate C—C bonds are proposed to be mediated by carbon radicals

generated via homogenous photoredox catalysis approaches.^{88, 99}

C(sp³)—C(sp³)/C(sp³)—C(sp²) Coupling

Early photocatalytic C(sp³)—C(sp³) coupling relied on amine coupling partners. Representative examples are the redox-neutral photochemical coupling of imines¹⁰⁰ or α -amino C—H (Fig. 4A)¹⁰¹ with benzylic and allylic C—H bonds. The proposed photoactivation mode is the reductive quenching of the photosensitizer by the amine substrate, giving an amine radical cation that can subsequently undergo fast deprotonation to yield an α -aminoalkyl radical, poised for radical C—C cross-coupling. Enantioselectivity can also be realized by either bifunctional chiral Ir(III)-type photocatalysis¹⁰² or dual photoredox and chiral ionic Brønsted acid catalysis.¹⁰³ Photoactivation has also been applied to C(sp³)—C(sp²) coupling with amine substrates such as tertiary amines¹⁰⁴ and inexpensive α -amino acids.¹⁰⁵

Recent breakthroughs in cross-coupling catalysis enable the use of coupling partners with substrates other than amines.¹⁰⁶⁻¹¹⁰ For instance, the coupling of aryl C(sp²)—H bond with benzylic¹⁰⁶ and allylic¹⁰⁷ C(sp³)—H bonds was successfully accomplished based on a dual photoredox and thiol organocatalytic protocol. More specifically, a transiently formed thiyl radical (generated by PCET oxidation of a thiol organocatalyst with an excited state photosensitizer) can engage in hydrogen atom abstraction from weak benzylic and allylic C(sp³)—H bonds, allowing for a radical coupling mechanism. Successful C(sp³)—C(sp²) coupling based on the use of pre-functionalized C(sp³) substrates that enable the photocatalytic generation of alkyl radicals, such as alkyl trifluoroborates¹⁰⁹ and alkyl potassium bis(catecholato) silicates,¹¹¹ have also been developed. Strategic use of non-

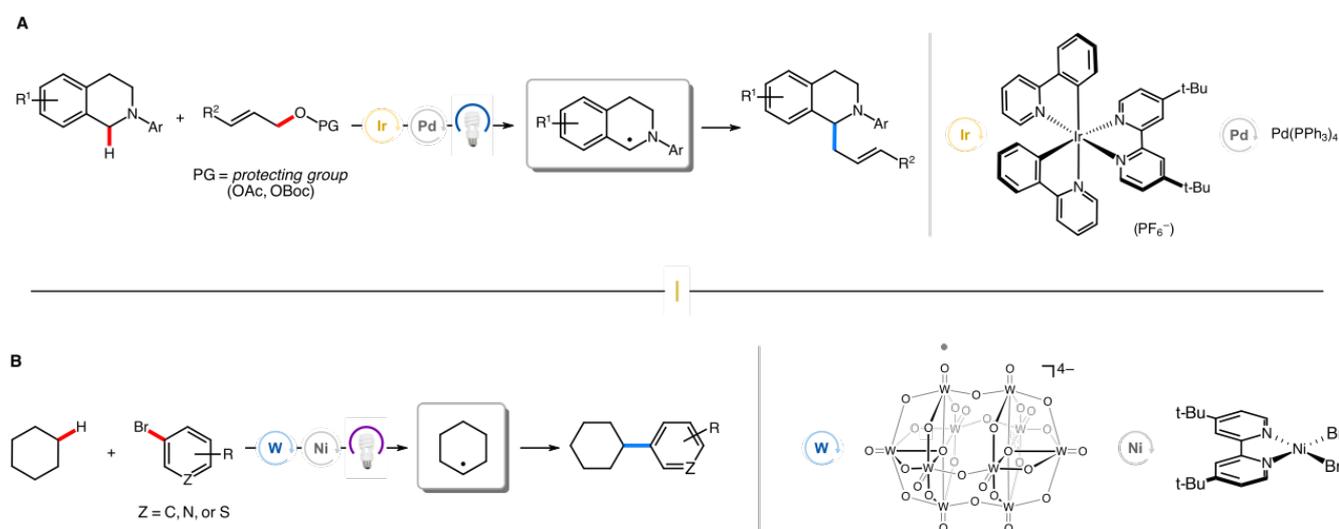


Fig. 4. Redox-neutral photocatalytic with C(sp³) radical intermediates. (A) C(sp³)—C(sp³) coupling between α -amino C—H allylic C—H initiated by blue-light excitation.¹⁰¹ (B) C(sp³)—C(sp²) coupling between cyclohexane and aryl bromide upon 390 nm excitation.¹⁰⁶

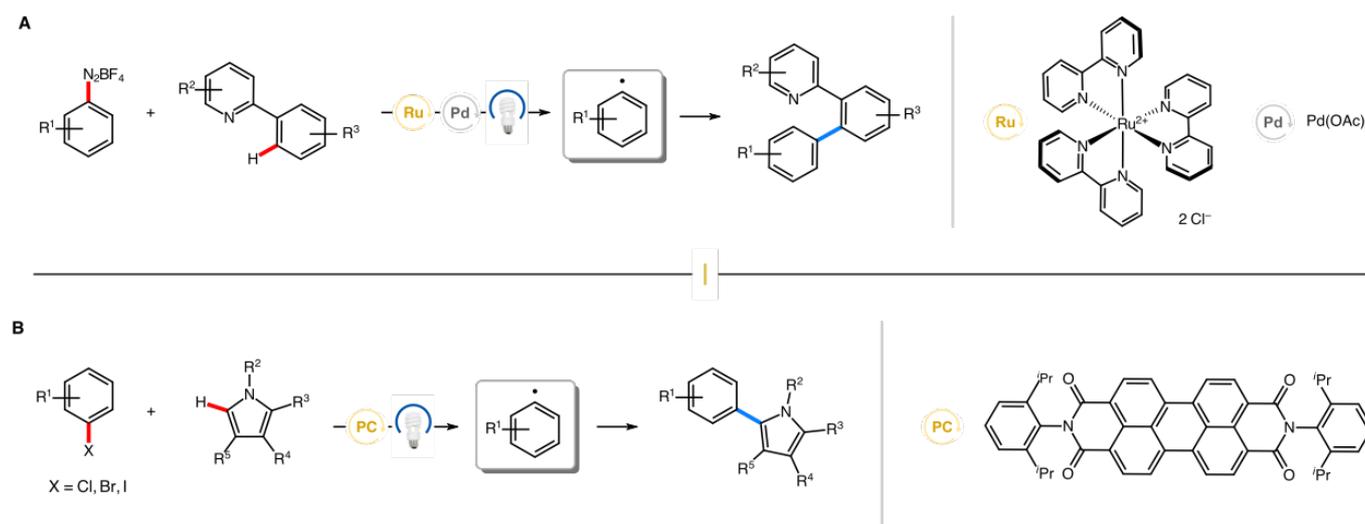


Fig. 5. Photocatalytic C(sp²)–C(sp²) coupling (A) via photoreduction of aryldiazonium salts¹¹⁶ with visible light and (B) photoreduction of aryl halides upon 455 nm excitation.²³

functionalized alkyl bromide substrates was made possible by incorporating stoichiometric tris(trimethylsilyl)silane for the in situ photochemical generation of silyl radicals and subsequent halogen abstraction of alkyl bromides to give alkyl radicals preceding carbon-carbon coupling.¹¹² Photocatalytic coupling between an aryl C(sp²) and non-functionalized strong aliphatic C(sp³)–H bonds proceeds through a C(sp³) radical intermediate, proposed to be generated via hydrogen atom abstraction by a decatungstate photooxidant. (Fig. 4B).¹¹³ A consecutive two-photon absorption process to forge C(sp³)–C(sp²) bonds between aliphatic substrates and aryl chloroformate has also been reported.⁸⁶ In the proposed mechanism, the first photon initiates the photooxidation of Ni(II)(CO₂R)(Cl) to Ni(III). The second photon brings the Ni(III) intermediate to its excited state that undergoes Ni–Cl homolysis to generate chlorine radicals that eventually abstract hydrogen from aliphatic substrates, yielding aliphatic C(sp³) radicals. The synthetic power of generating C(sp³) radicals with photoexcitation is further demonstrated by engaging sunlight-mediated gold-catalyzed coupling with 1-iodoalkynes to forge C(sp³)–C(sp) bond using amines as the C(sp³) source.¹¹⁴ Broad substrate scope with respect to both coupling partners was realized, including multi-substituted amines and iodoalkynes with electron-donating and electron-withdrawing groups.

C(sp²)–C(sp²) Coupling

C(sp²) radicals are usually less stable than C(sp³) radicals; as a result, generation of C(sp²) radicals requires harsher conditions or a more complex pre-functionalized structure. Taking inspiration from the Meerwein arylation addition reaction,¹¹⁵ one approach to the photochemical generation of C(sp²) radicals is based on the photoreduction of aryldiazonium salts, resulting in the release of nitrogen and concomitant generation of aryl radicals.⁸⁸ The aryl radicals can then be used to forge C(sp²)–C(sp²/sp) bonds with other unsaturated carbon sources such as unfunctionalized arenes (Fig. 5A),¹¹⁶ heteroarenes,¹¹⁷

alkenes, enones, and alkynes in good yields.^{66, 118} A consecutive two-photon approach to generate aryl radicals directly from aryl bromides and chlorides and C(sp²)–C(sp²) coupling with substituted pyrroles was achieved using perylenebisimides (PDI) (Fig. 5B).²³ The first photon initiates the photoreduction of PDI by sacrificial reagents to generate an intermediate PDI radical anion. The singly-reduced PDI, a strong photoreductant, then absorbs another photon and accomplishes the reduction of aryl bromides and chlorides that subsequently releases halide anions to give aryl radicals.

C–N Bond Formation

Reactions that can forge a C–N bond are particularly relevant for the pharmaceutical industry, as over half of the top 100 best-selling drugs in the US have at least one C–N bond in their structure.¹¹⁹ It is, then, not surprising that much research effort has been focused on these reactions. However, C–N bond formation is less relevant than C–C and C–O formation for the production of fuels and feedstocks and is not discussed in detail herein. Amination of arene C(sp²)–H bonds, including protected phenols, haloarenes and nitrogen heteroarenes, was realized using acridinium as a photooxidant with O₂ as the sacrificial electron acceptor (Fig. 6A).¹²⁰ Direct cyanation of arene C(sp²)–H bonds was reported under similar conditions.¹²¹ Intramolecular coupling between an amide and ketone (Fig. 3) is initiated by an Ir(III) photooxidant.⁹⁷ Thermal, palladium-catalyzed C–N cross-couplings developed by Buchwald and Hartwig^{122, 123} have been applied in industrial settings. More recently, Buchwald and MacMillan reported a photocatalyzed alternative to prepare anilines (Fig. 6B).¹²⁴

Selective Oxidation of Alcohols, Arenes, and Alkanes

Selective oxidation of molecules with several different functional groups poses great challenges for fine chemical manufacturing. Industrial oxidation of alcohols, for example,

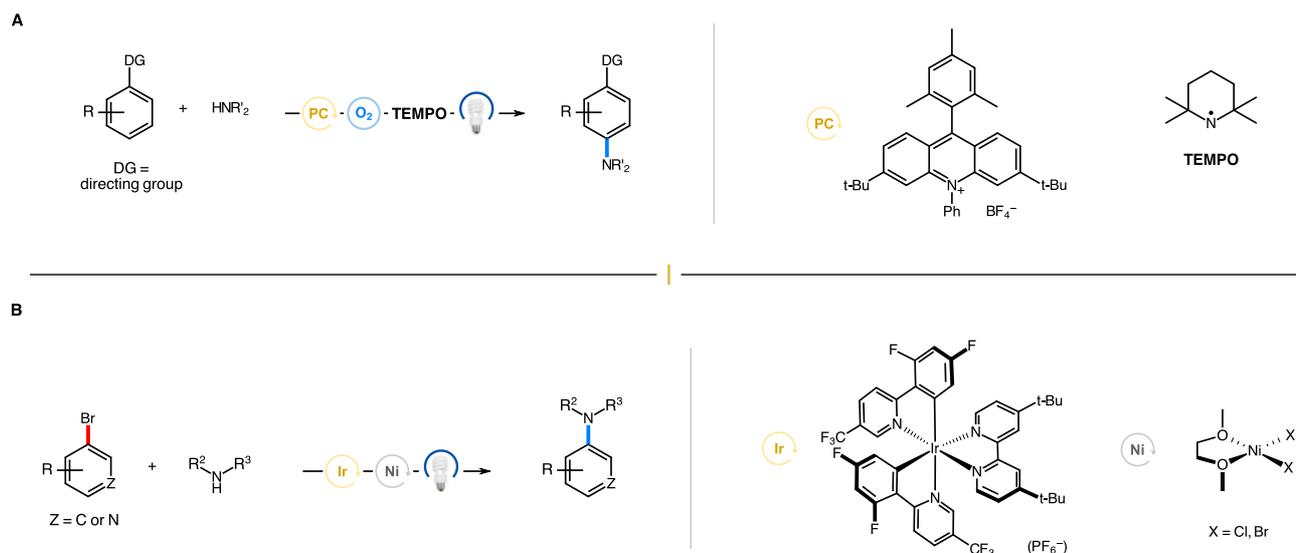


Fig. 6. Photocatalyzed C—N bond formation **(A)** with acridinium as a photooxidant upon 455 nm excitation¹²⁰ and **(B)** with blue-light excitation of an Ir(III) photosensitizer to produce anilines.¹²⁴

employs stoichiometric quantities of energy-intensive oxidants such as chromates, permanganates, and organic peroxides to reach satisfactory yields and selectivity (specifically avoiding over-oxidation).¹²⁵ Exploitation of photocatalytic approaches would allow for not only milder and greener conditions that require lower energy input but also better selectivity for accomplishing these oxidative transformations.

Alcohol Oxidation

Partial oxidation of alcohols to aldehydes and/or ketones via heterogeneous photocatalysis is a well-studied reaction. TiO₂-based photocatalysts with UV light irradiation are powerful oxidants, which lowers their chemical selectivity towards partially oxidized products.^{126, 127} By sensitizing TiO₂ with CdS quantum dots, the oxidizing power in the active sites is minimized.¹²⁸⁻¹³⁰ As a result, high selectivity was realized, enabling the partial oxidation of benzylic alcohols to aldehydes (Fig. 7A).¹²⁹ Moreover, the replacement of TiO₂ with other types of semiconductors such as metal sulfides,¹³¹⁻¹³³ bismuth-containing semiconductors,^{134, 135} and metal-free graphitic carbon nitrides¹³⁶⁻¹³⁸ due to their milder oxidizing power, also leads to improved selectivity and yields. Selective oxidation of alcohols via homogeneous photocatalysis takes advantage of the high redox power on the excited state of the photocatalyst to generate reactive oxygen species (ROS) such as superoxide anion radical, hydrogen peroxide, or singlet oxygen, which have many applications in oxidative organic reactions.^{139, 140} Photocatalysts based on metals such as Ir, Cu, Pt, and a functionalized porphyrinic metal organic framework (MOF) were reported to show oxidative reactivity for benzylic and allylic alcohols.¹³⁹⁻¹⁴² In 2018, a metal-free catalyst, fluorenone, was reported to achieve photocatalytic oxidation of aliphatic, heteroaromatic, and alicyclic alcohols to their corresponding

aldehydes or ketones using oxygen as the oxidant (Fig. 7B).¹³⁰ A superoxide anion radical intermediate was proposed.

Arene Oxidation

The cumene-phenol process that chemical industries use to produce phenol from benzene has an energy cost of five billion kWh/yr in the United States.² Photochemical hydroxylation of benzene to phenol is a promising strategy to help decrease the cost of this transformation. The difficulty with this approach is selectivity, as phenol is thermodynamically easier to oxidize than benzene.¹⁴³ In photocatalytic systems, semiconductors have been used as light absorbers as well as the platform that supports the oxidation processes,¹⁴⁴⁻¹⁴⁷ combined with a variety of oxidants, such as nitrogen oxides, molecular oxygen, or H₂O₂. Selectivity and activity could not be simultaneously optimized until it was realized that further oxidation of phenol could be avoided by accelerating the desorption of phenol.¹⁴⁸ Guided by this idea, the surface of TiO₂ was silylated to make it hydrophobic, leading to the enhancement of both activity and selectivity (Fig. 7C).¹⁴⁹

Selective oxidation of primary C(sp³)—H bonds has great potential in applied chemistry to produce value-added products from natural petroleum.¹⁵⁰ One such example is the oxidation of toluene to benzaldehyde, which was reported using TiO₂ as a photocatalyst under UV irradiation, albeit with poor performances.¹⁵¹ Blocking the active sites on the TiO₂ surface with less active WO₃ lead to increased selectivity and activity¹⁵² Further improvement of the photocatalytic performance for this transformation was achieved by replacing TiO₂ with cadmium based¹⁵³ and bismuth-based materials.^{154, 155} Another reaction of industrial interest is the partial oxidation of cyclohexane to cyclohexanol and cyclohexanone. Satisfactory reaction performance with minimum over oxidation was realized using a similar strategy as the photocatalytic

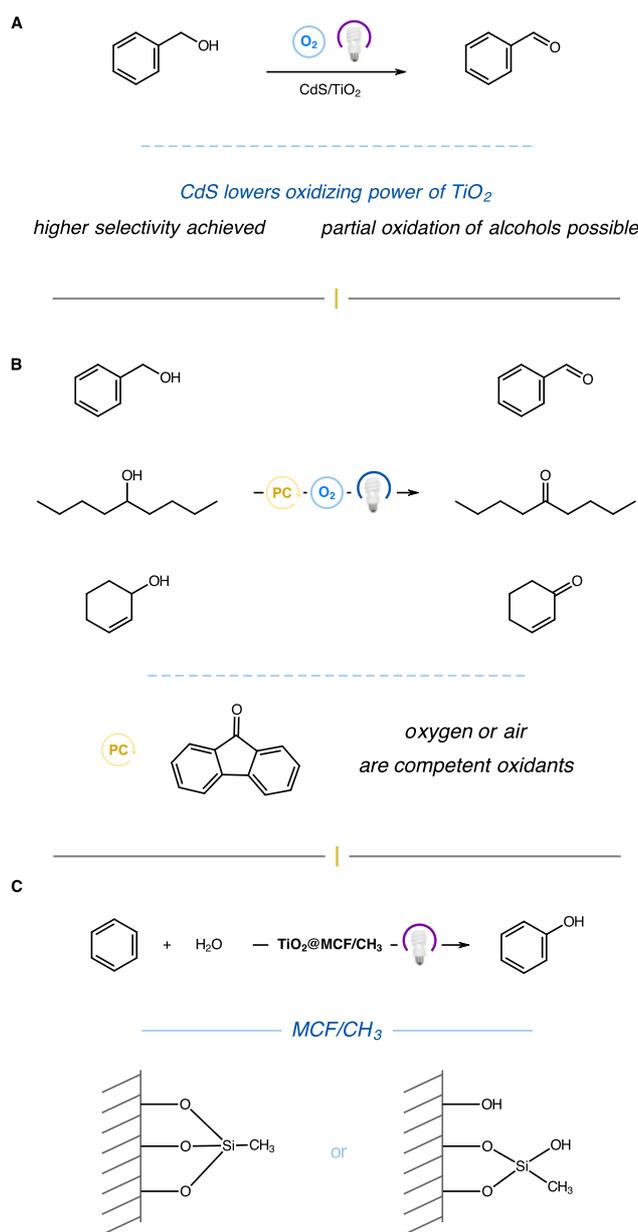


Fig. 7 Photocatalyzed oxidation of alcohols (A) with visible-light (>420 nm) excitation of CdS nanoparticles on TiO₂,¹²⁹ (B) with fluorenone as an organic photocatalyst with blue-light excitation.¹³⁰ (C) A hydrophobic surface on TiO₂ minimized a phenol oxidation side reaction upon UV (>320 nm) irradiation.¹⁴⁹

hydroxylation of benzene. The surface of TiO₂ was modified with trimethylsilane (HSi(CH₃)₃) to increase its hydrophobicity, as this leads to fast desorption of partially oxidized products.¹⁵⁶ Other types of semiconductors such as bismuth-containing¹⁵⁷ or metal-free semiconductors^{158, 159} with certain degrees of hybridization across categories also demonstrated promising activity and selectivity for this transformation.

Alkane Oxidation – Homogeneous Photocatalysis

Homogeneous photocatalytic oxidation of alkanes can be categorized as a C(sp³)—H functionalization reaction. A large

portion of C(sp³)—H functionalization has been discussed in the C(sp³)—C(sp³/sp²) coupling section. In terms of the coupling with heteroatoms, benzylic C(sp³)—H functionalization to form C—N and C—O bonds has been achieved via visible light photoredox catalysis.^{160, 161} When subjected to different coupling partners (water versus secondary amines), benzylic C(sp³)—H bonds can be selectively oxidized to the corresponding carbonyl or alpha-aminated compounds using an iridium photooxidant (Fig. 8A).¹⁶¹ This species was proposed to oxidize the benzylic substrates after photoexcitation, leading to formation of a benzylic alpha cation which is then attacked by a nucleophile such as water or tertiary amines. Another important oxidative transformation for alkanes is dehydrogenation to produce alkenes, which serve as one of the central functional groups in organic synthesis, valued in both industrial^{162, 163} and laboratory transformations.¹⁶⁴⁻¹⁶⁸ A homogenous dual photocatalytic strategy was recently demonstrated.^{169, 170} Tetra-n-butylammonium decatungstate (TBADT) was used to photochemically abstract a hydrogen atom from alkanes to yield C(sp³) centered radicals. Taking inspiration from the hydrogen-evolving bio-cofactor adenosyl cobalamin fragment, a cobaloxime co-catalyst was added to suppress the bimolecular radical coupling side-reactions by abstracting the highly labile hydrogen atoms adjacent to the C(sp³) radicals upon their generation to give the desired alkene products. Proof-of-concept experiments in which cyclooctane and cyclopentane were reduced to give the corresponding ene products demonstrated the practicality of the proposed cooperative HAT mechanism (Fig. 8B).¹⁷⁰

Enzyme Catalysis

Biocatalysis, which uses nature-derived catalysts such as enzymes or whole cells, is an emerging alternative to traditional metal or organocatalysis in chemical synthesis, offering high catalytic rate under environment-friendly conditions with unparalleled specificity.^{171, 172} However, the narrow substrate scope resulting from the high specificity of substrate-enzyme interactions has been a hurdle in expanding the use of enzymes to non-natural chemical reactions.¹⁷³ Several different approaches have been utilized to overcome this limitation. First, developments in protein engineering techniques enabled optimization of the properties of enzymes in a targeted manner.¹⁷⁴⁻¹⁷⁸ In parallel, efforts have been devoted to chemoenzymatic catalysis strategies that combine the selectivity of biocatalysis with the reactivity of chemocatalysis.¹⁷⁹⁻¹⁸¹ This includes development of artificial metalloenzymes that combine the versatility of homogeneous transition metal catalysts and the specificity of the enzymatic protein scaffold, which has been improved upon by directed evolution methods.¹⁸²⁻¹⁸⁴ However, challenges in reconciling the vastly different reaction conditions for biocatalysts and chemical catalysts have limited the repertoire of chemo-biocatalysis to a narrow class of reactions.^{185, 186}

With the recent resurgence of interest in photoredox catalysis and its higher compatibility with enzyme-controlled reactions, the merger of (chemo-)biocatalysis with photocatalysis, i.e.

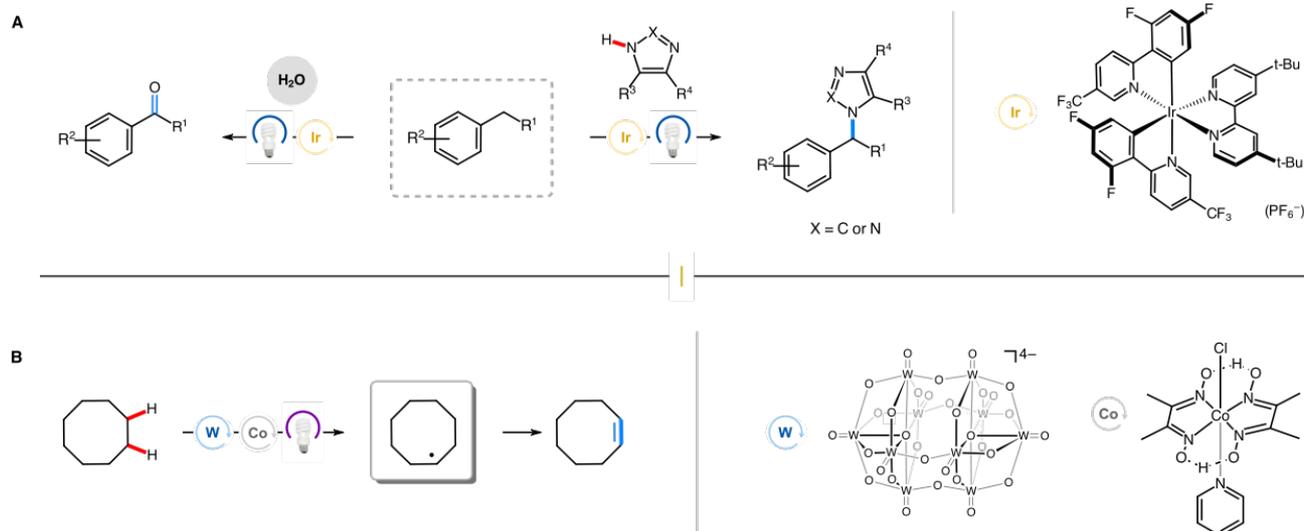


Fig. 8. Photocatalytic direct oxidation of alkanes: (A) oxidation of C–H bonds into C–O/N bonds by an Ir(III) photocatalyst upon blue-light excitation,¹⁶¹ and (B) alkane dehydrogenation to olefin with TBADT photosensitizer and cobaloxime catalyst upon UV excitation.¹⁷⁰

photobiocatalysis, is being increasingly explored as a potential solution to the aforementioned limitations. Although typical enzyme function is thermally activated, several known enzymes exhibit native light-driven reactivity. These include protochlorophyllide-reductases responsible for chlorophyll biosynthesis,^{187, 188} photolyases that drive DNA repair,^{189, 190} and photodecarboxylases that catalyze conversion of fatty acids to alkenes and alkanes.^{191, 192} While these native systems offer some degree of variability, they generally operate by either direct or indirect excitation of the cofactor or substrate in order to initiate photochemistry. This mechanistic diversity is extended in the case of synthetic photobiocatalysis routes and includes electron transfer mediated cofactor regeneration, formation of catalytic intermediates in reaction cascades, and enhanced catalytic ability for light-driven enzyme promiscuity. In the most common application of photobiocatalysis, the prohibitively expensive cofactor of oxidoreductases, such as NAD(P)H/NAD(P)⁺, are regenerated with photocatalysis to enhance the efficiency of native biocatalytic reactions.¹⁹³ The reaction proceeds by using photocatalytically generated redox equivalents (formed outside the protein) to drive biocatalytic conversion.^{194, 195} Here, a photosensitizer accepts electrons from a sacrificial electron donor, and the subsequent direct or mediated electron transfer regenerates the cofactor (Fig. 9A).¹⁹⁶ A wide range of photosensitizers have been utilized in this approach including transition metals, quantum dots, molecular dyes, and flavins.¹⁹⁷ Examples of successful photoactivation have been reported for a range of oxidoreductases such as (de)hydrogenases, nitrogenases, cytochrome P450s, and flavin-dependent enzymes, which catalyze reactions including hydrogenation, hydroxylation, and Baeyer-Villiger oxidation.¹⁹⁷

Another approach for combining photocatalysis and (chemo-)biocatalysis is by forming reaction cascades, where the photocatalytic step directly contributes to the formation of the product, unlike in the previous approach. Here the photocatalytic step and biocatalytic step (or vice versa) are sequential, resulting in formation of an intermediate species

that serves as the substrate for the final step (Fig. 9B). This leads to a reaction scheme in some cases allowing for “one-pot” synthetic routes.^{198, 199} Although only few examples have been reported thus far, improved yields and enantioselectivity were achieved in isomerization/reduction of olefins,²⁰⁰ C–H functionalization,^{201, 202} and synthesis of 1,3-mercaptoalkanol.²⁰³ The complexity of this method has also been extended to multi-enzyme cascades allowing for a cofactor regeneration step in the case of isobutanol generation and water oxidation (Fig. 9).^{204, 205}

Non-Native Enzyme Catalysis

Photocatalysis can be coupled with catalytically promiscuous enzymes to power novel, non-natural functions beyond their native roles expanding the applications of photobiocatalysis (Fig. 9C). Among the most commonly utilized classes of enzymes with catalytic promiscuity are hydrolases due to their high stability in organic solvents and lack of need for cofactors.²⁰⁶ The first example of merging non-natural activity of hydrolases with photocatalysis was reported for wheat germ lipase combined with [Ru(bpy)₃]²⁺ under fluorescence lamp illumination, which enabled one-pot, enantioselective synthesis of indolone.²⁰⁷

Oxidoreductases are another class of enzymes shown to be capable of unlocking unprecedented non-natural reactivities. The catalytic activity of oxidoreductases depends on cofactors in their redox-active center, such as metal ions or complexes, amino acid residues, and organic molecules like nicotinamide (NAD(P)) and flavin (FMN, FAD) derivatives.²⁰⁸ Photoexcitation of nicotinamide and flavin cofactors within the active site results in formation of novel radical intermediates, which enables challenging organic transformations with high enantioselectivity due to the specificity of the enzymatic scaffold. In one example with nicotinamide-dependent ketoreductases (KREDs), the radical intermediate served as a chiral hydrogen atom source for dehalogenation of lactones.²⁰⁹ A similar mechanism was utilized in a series of flavin (FMN)-dependent “ene”-reductases (EREDs) to grant access to

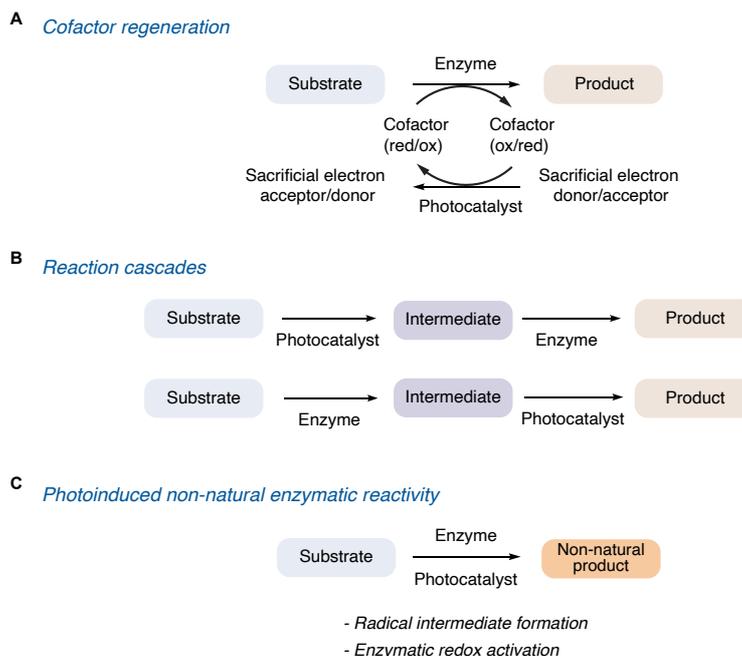


Fig. 9. Mechanisms of photobiocatalysis. (A) Light-assisted regeneration of enzyme cofactors. (B) Formation of photobiocatalytic reaction cascades. (C) Non-natural reactions enabled by promiscuous enzymes and photocatalysis.

enantioselective reductive cyclization of chloroamides to produce lactams.²¹⁰ In both cases, mechanistic studies revealed that the radical intermediate was produced via formation of an electron donor-acceptor (EDA) complex between the substrate and the cofactor within the active site. The EDA complex subsequently undergoes a single-electron transfer event upon photoexcitation into the charge transfer band. A more recent example demonstrated that EREDs can also catalyze redox-neutral radical cyclizations to produce enantioenriched oxindoles, a C-C bond forming reaction.²¹¹ Unlike in previous work,²¹⁰ where flavin hydroquinone (FMN_{hq}) was the reactive state of cofactor that was photoexcited within an EDA complex, light irradiation directly prepares a semiquinone state of flavin (FMN_{sq}) without the involvement of an EDA complex.

Exogenous photocatalysts in the active site of enzymes have also been explored. This approach takes advantage of the enhanced reactivity brought about by hydrogen bonding interactions that take place between the substrate and the active site, known as “enzymatic redox activation”.²¹² These interactions are thought to tune the reduction potential of the substrate, thereby enhancing the efficiency of photocatalytic cycles. Initial investigations reported increased catalytic efficiency of xanthene-based photocatalysts, Rose Bengal and Eosin Y, and [Ru(bpy)₃]²⁺ in the active sites of nicotinamide-²¹³ and flavin-dependent²¹⁴ enzymes, respectively.

Future Directions

Research investment in photocatalysis for feedstock chemicals and fuels has the potential to evolve the chemical manufacturing industry to meet growing demand with minimized environmental impact. Photocatalysis is an immensely powerful approach toward chemical transformations. Artificial photosynthesis, photocatalytic

nitrogen fixation, and photocatalysis in pharmaceutical manufacturing have tremendously benefitted from photocatalysis research.²¹⁵⁻²¹⁷

To meet the needs of chemical manufacturing, cost and scale must be addressed. Chemical feedstocks are produced at immense scale with negligible profit margin.¹⁶ Chemical feedstock manufacturing typically passes petrochemical feedstocks over zeolite catalysts at elevated temperature and pressure at refineries that have been in operation for decades. The long-term benefits of solar manufacturing must be superior to traditional methods. Maximizing the efficiency and recoverability of photocatalysts and utilizing waste rather than petrochemicals as feedstocks can mitigate the costs of solar manufacturing. However, because feedstock chemicals are essentially sold at production cost, innovation of cost structure is needed to develop and install solar manufacturing. Policy incentives that favor low-carbon industry and that support repurposing biowaste and single-use plastics would make photocatalysis an appealing alternative to petrochemical feedstock production.

Expanding the scope of photocatalysis to chemical manufacturing would lessen the process fuel requirement and increase the accessibility of alternative feedstock sources. Photocatalysts can selectively access high-energy intermediates, negating the high temperature and pressure reaction conditions of many traditional catalysts, often with improved yields. Improved selectivity likely corresponds with a greater product output per energy input ratio. Photon quantum yields must be reported for photocatalyzed reactions to benchmark efficiency.

Selective depolymerization of lignin and synthetic polymers provides alternative feedstock sources. Further photocatalysis development for aromatic demethoxylation and phenol

reduction would transform lignin monomers into benzene, toluene, and xylene (BTX), some of the most energy-intensive petrochemical feedstocks. Photocatalyzed coupling of small molecules to produce longer chain hydrocarbons would provide solar fuels that are compatible with current infrastructure.

Ongoing challenges to photocatalysis include efficient, broad-spectrum light absorption, rapid decay of excited states, charge recombination following excited state oxidation or reduction, and achieving selective catalysis at highly oxidizing and highly reducing thermodynamic potentials.

The activity of a number of common photocatalysts and photosensitizers is limited by a small absorption cross-section.⁸⁹ One emerging strategy to overcome this limitation is to couple natural photosynthetic systems into the catalytic system. The large absorption cross-sections of natural photosynthetic systems brought about by the large number of the light-harvesting pigments therein enable higher-efficiency photon capture and, in turn, catalysis of chemical transformations.²¹⁸ Photosynthetic light-harvesting systems and isolated photosynthetic pigments have been successfully used to photosensitize a number of reactions including hydrogen evolution, glucoside biosynthesis, cyclization, and polymerization.²¹⁹⁻²²⁶ Progress in developing these platforms for bio-hybrid photoredox chemistry has the potential to serve as a route for efficient generation of value-added products.²²⁷⁻²²⁹ Photosynthetic light-harvesting complexes could be utilized to enhance photocatalysis via photon capture and subsequent energy transfer, similar to fluorophore-based energy transfer mediated catalysis.²³⁰

Increasing excited-state lifetimes of earth abundant photocatalysts is important for the development of industrial-scale photocatalysis. Rigid, multi-dentate ligands are typically necessary with first-row transition metal photocatalysts to achieve the nanosecond to microsecond excited states lifetimes required for bimolecular processes.^{231, 232} Another approach to extend excited-state lifetimes is to use donor-acceptor ligands that promote formation of a charge-separated excited state.²³³⁻²³⁶ Detailed knowledge of the photophysics of a photosensitizer is important for molecular modifications. Guided by excited-state coherence data, synthetic modifications to an Fe(II) photosensitizer increased the excited-state lifetime by twentyfold.²³⁷

Charge recombination following photoinitiated oxidation or reduction of substrate limits reaction quantum yields. Charge recombination is usually diffusion-limited and can be faster than the forward charge transfer process.²³⁸ Appendage of electron-donor and acceptor ligands to molecular photosensitizers can slow the rate of recombination.^{239, 240}

Achieving selective bond activations at strongly reducing and strongly oxidizing potentials will broaden the scope of photocatalysis. Electrode-primed photoredox catalysis, the photoexcitation of electrochemically reduced catalysts, demonstrates selectivity at strongly reducing potentials.^{41, 241, 242} A similar approach may be applied to bond activations at highly oxidizing potentials.^{243, 244}

Addressing the massive scale needed for solar manufacturing requires transdisciplinary efforts that combine photocatalysis

with forward-looking engineering to advance photoreactor designs and optimize solar energy harvesting. Coupling solar concentration technology with photoreactors, for example, allows for small and controllable reactor size for chemical handling while simultaneously maximizing solar collection. Several different concentrator concepts have been considered for use in the detoxification of chemically contaminated water.²⁴⁵ Tubular flow photoreactors are often mounted on the focal line of a parabolic trough reflective surface that collect and concentrate solar irradiation, which increases the number of photons per reaction volume. The tube reactor helps sustain pressure and flow levels required by circulation systems for photocatalytic wastewater treatment. Although solar water treatments have made significant progress in research and industrial application, other solar catalytic technologies remain less developed. More efforts are required in both fundamental science and engineering to achieve efficient and cost-effective solar manufacturing.

The greatest challenges for actualizing solar manufacturing are maximizing light absorption, minimizing excited state relaxation and charge recombination deactivation processes, and achieving higher energy bond activations without losing selectivity. Catalyst cost and ease of recovery are essential considerations. Given the trajectory of research discoveries in the field, we envision solar manufacturing building on the fundamental science of photocatalysis to sustainably meet the growing demand for chemical products.

Author Contributions

The introduction, and non-petrochemical feedstocks were written by HJS. General mechanisms for photocatalysis were written by LT, XL, and HJS. Hydrocarbon oxidation, C–C, and C–N bond formation review by LT. Enzyme catalysis review by MS and SMH. Future directions were written by HJS, SMH, and XL. Fig. 1 by XL and HJS. Concept for Fig. 2 by DMAR and photos by HJS. Fig. 3 by HJS and edited by DMAR. Figures 4-8 by LT and edited by DMAR. Fig. 9 by MS. All authors read and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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