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Unleashing the potentiality of metals: synergistic catalysis with light and electricity

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The integration of transition metals as catalysts has opened new avenues for organic synthesis, including the activation and formation of diverse bonds. The combination of metal catalysis with photochemistry or electrochemistry has demonstrated enhanced reaction selectivity and reduced reliance on chemical oxidants. By harnessing the potential of organic photo-electrocatalysis, which combines photocatalysis with electrocatalysis, a wide range of efficient, selective and sustainable synthetic transformations have been achieved. This review provides a comprehensive overview of metal catalysis in photo-electrochemical systems, discussing reaction mechanisms and offering prospects for this triadic catalytic mode.

1. Introduction

Transition metals are widely distributed in the Earth's crust.¹ They are not only essential trace elements for all life forms² but also serve as catalysts in organic reactions, providing new modes of chemical activation.³ For instance, the 2010 Nobel Prize was awarded to Heck, Negishi, and Suzuki for their contributions to palladium-catalyzed cross-coupling reactions.⁴ With further research, significant progress has been made in transition metal-catalyzed C–H alkylation of alkenes,⁵ C–N bond formation,⁶ and C(sp³)–H activation.⁷ Simultaneously,

with photocatalysis gaining popularity, visible-light-induced transition metal catalysis has garnered increasing attention.⁸ In this context, transition metals may play a dual role:⁹ (a) absorbing light energy (photons) as photocatalysts; (b) catalyzing the bond cleavage and formation through either traditional or novel mechanisms. Therefore, by harnessing the unique reactivity of transition metal complexes in their electronically excited states, fundamental organometallic reactions such as oxidative addition, reductive elimination, β -hydrogen elimination, and bond cleavage can be achieved under irradiation.¹⁰ One common strategy is ligand-to-metal charge transfer (LMCT), and research has been particularly intensive in recent years due to the use of cost-effective and readily available metals like iron, copper and nickel.¹¹

In contrast, rare earth metals, despite being important elements, have been less explored in the field of synthesis. This may be attributed to the fact that most rare earth metals predominantly exist in stable oxidation states, making them

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less prone to the typical two-electron redox reactions observed in other transition metals.¹² Nonetheless, in recent years, rare earth (RE) metal-based catalysts have also made advancements in multifunctional C–H functionalization reactions.¹³ Cerium (Ce) is the most abundant element among rare earth metals. Industrially, cerium is primarily used in fluorescent materials and industrial exhaust gas treatment. In synthetic chemistry, it is often employed as a Lewis acid and oxidant.¹⁴ In 2018, Zuo *et al.* explored the optical properties of cerium complexes and generated highly active alkoxy radical species through LMCT processes, thereby initiating subsequent reactions.¹⁵ Building on this initial inspiration, researchers have extended cerium photocatalysis to areas such as C–H activation, alcohol hydroxyl group activation, and decarboxylation.^{11b,16}

The electrostatic interactions delineated by the mutual attraction between electrons and atomic nuclei represent a pivotal force integral to the framework of electrochemistry. This intricate force not only governs but also modulates the nuanced interactions between electrons and atomic nuclei, thereby endowing redox reactions with their distinctive potential.¹⁷ Organic electrochemical synthesis emerges as a sophisticated and environmentally conscious approach to organic synthesis. It offers refined and controlled reaction conditions, harnessing pristine electrical energy in lieu of conventional oxidants, thereby epitomizing the contemporary pursuit of sustainable and green chemistry.¹⁸ Integrating transition metal catalysis with electrochemistry addresses longstanding challenges in chemical synthesis. This approach not only enhances selectivity but also circumvents the use of stoichiometric chemical oxidants, aligning with the principles of atom economy that are increasingly sought after.¹⁹

With the flourishing development of photocatalysis and electrocatalysis, the emerging strategy of organic photo-electrocatalysis (EPC), which combines photocatalysis with electrocatalysis, has gained momentum.²⁰ In this novel reaction paradigm, photo-electrocatalysis maintains the distinctive characteristics of both disciplines while achieving complementary

synergy. Utilizing light energy can reduce the reaction potential, and by modulating the current, cathodic reduction and anodic oxidation can be orchestrated. This can effectively enhance reaction efficiency and reduce energy consumption.²¹

To enhance the catalytic activity of metals and broaden their range of reactions, in addition to using metal complexes as photocatalysts or incorporating them into electrochemical applications as previously mentioned, there is also a strategy to promote reactions through synergistic catalysis involving metal-photosensitizer/ligand combinations.²² In this paper, we will focus on another currently popular strategy that combines metal catalysis with both photo- and electrochemical methods. This triadic catalytic mode significantly unleashes the potential of metal catalysis, and since 2020, this type of reaction has begun to gain prominence. To provide researchers with a clearer understanding of the performance of metals in photo-electrochemical systems, this review comprehensively summarizes the relevant studies. Based on the different metals used, the reactions are categorized into five groups: (1) iron catalysis, (2) copper catalysis, (3) cerium catalysis and (4) other metal catalysis. Additionally, the review discusses some reaction mechanisms, substrate scopes, and offers prospects for this triadic catalytic mode.

2. Iron-catalyzed photo-electrochemical reactions

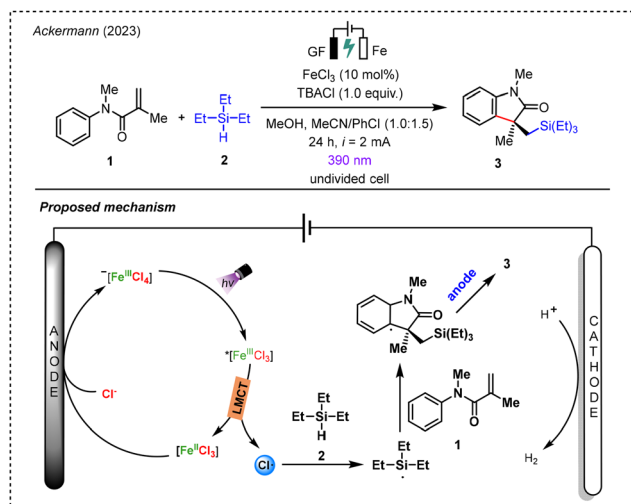
Since the early 1920s, iron-catalyzed reactions have gained increasing attractiveness. Iron catalysts, being first-row transition metals, typically exhibit single-electron transfer (SET) processes in cross-coupling reactions.²³ Luminescent Ru(II) and Ir(III) polypyridyl complexes exhibit long-lived excited states with redox activity.²⁴ In recent years, efforts have been devoted to enhancing the excited-state lifetimes of iron complexes to achieve more efficient photo-reactivity.^{1d,25} However, increasing the excited-state lifetime is not the sole approach to realizing useful photo-reactivity of iron complexes. Under visible light irradiation, the direct coordination of organic substrates to iron, facilitating intramolecular charge transfer, known as the LMCT (ligand-to-metal charge transfer) process, has emerged as a current research hotspot.¹¹ Researchers have developed iron photocatalyzed reactions such as C–H activation, decarboxylation, and alcohol activation.²⁶ To further expand this reaction type, the LMCT system has also been extended to electrochemistry. Next, the focus will be on introducing the application of iron catalysis in photo-electrochemical reactions.

Organosilanes represent a unique moiety in medicinal chemistry and materials science, serving as versatile intermediates in molecular synthesis.²⁷ In 2023, the research group led by Ackermann achieved the iron-catalyzed activation of inert Si–H and Ge–H bonds under photoredox catalysis, as depicted in Scheme 1.²⁸ This process harnesses chlorine radicals generated by visible light-induced ferric chloride to hydrogenate inert silicon-based compounds, with the resulting



Binbin Huang

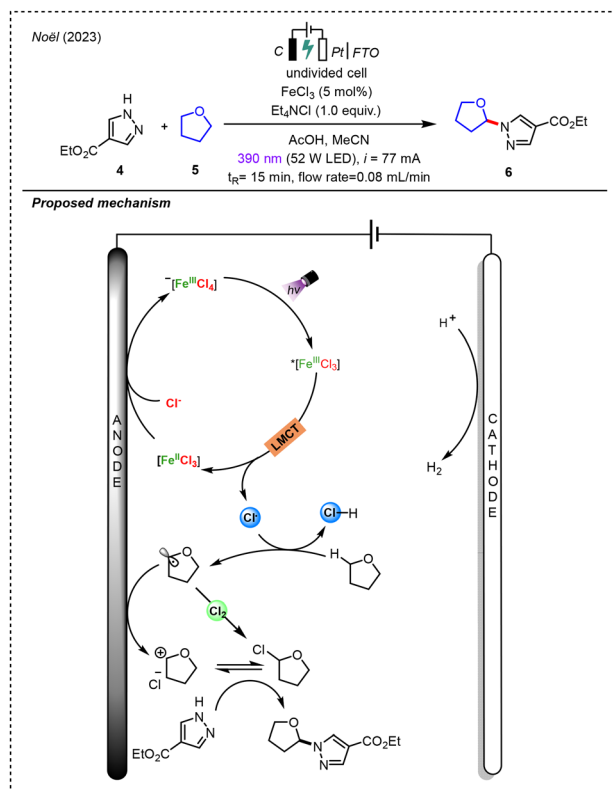
Binbin Huang obtained the bachelor's degree from Zhejiang University in 2014. Next, he acquired both the master's (2016) and PhD degree (2021) under the supervision of Prof. Wujiong Xia at Harbin Institute of Technology. After graduation, he took a position in Beijing Normal University at Zhuhai. His research interest mainly focuses on the development of sustainable organic synthetic protocols that are enabled by photo- and electro-chemical methods.



Scheme 1 Photo-electrochemical Si–H and Ge–H activation by iron catalysis.

silicon radicals attacking Michael acceptors to undergo subsequent cascade reactions, forming the desired compounds. Simultaneously, the anode facilitates the oxidation cycling of low-valent iron. This method exploits the photoinduced ligand-to-metal charge transfer (LMCT) and hydrogen atom transfer (HAT) processes of iron(III) complexes to achieve polarity-matched Si–H and Ge–H activation, selectively affording a wide range of silicon compounds with outstanding chemical selectivity.

To expand the scope of C(sp³)-N bond-forming reactions using HAT photocatalysis, Noël and colleagues employed decatungstate to facilitate hydrogen atom transfer (HAT) from the α -hydrogens of oxygen or nitrogen, generating carbon-centered radicals. Subsequent oxidation of these radicals leads to carbocations, which can readily be captured by *N*-heteroaryl reagents, thereby forming the targeted carbon–nitrogen bond.²⁹ Based on this foundation, in 2023, Noël further reported the accelerated electro-photocatalytic C(sp³)-H heteroarylation achieved using iron(III) chloride as a catalyst in an efficient continuous-flow reactor setup (Scheme 2).³⁰ The possible mechanism of the reaction is as follows: firstly, the chlorine ligand binds to the iron center to form a tetrachloroiron complex, which then absorbs violet light and transitions to an excited state. Subsequently, the Fe–Cl bond undergoes homolytic cleavage, producing chlorine radicals and reduced Fe(II) species. Afterwards, the reduced catalyst oxidizes at the anode to form Fe(III) center, thus completing the catalytic cycle. Iron plays a crucial role in this transformation, effectively suppressing undesired chlorination side reactions. Chlorine radicals undergo cleavage on adjacent heteroatoms (such as O, N, or S) of C–H bonds, generating nucleophilic carbon-centered α -oxyalkyl radicals. This radical intermediate is electrochemically oxidized to form a stable electrophilic carbon cation intermediate, which is subsequently trapped by a nucleophilic reagent to form the desired C–N bond. However, this method

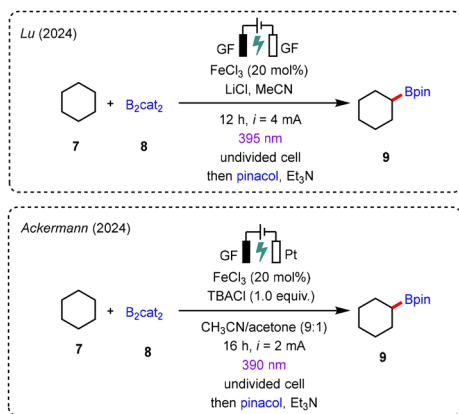


Scheme 2 Accelerated photo-electrocatalytic C(sp³)-H heteroarylation enabled by an efficient continuous-flow reactor.

cannot be extended to unactivated aliphatic C(sp³)-H bonds, indicating that only stable radicals can be oxidized.

In recent years, the study of C(sp³)-H borylation of inert alkanes under mild conditions has received widespread attention. In 2020, Aggarwal and colleagues reported the first example of visible light-induced C(sp³)-H borylation of inert alkanes without the need for metals or directing groups.³¹ In 2023, the Xia group reported an iron-catalyzed C(sp³)-H borylation reaction, which exhibited a broad substrate scope and excellent terminal selectivity, with the HAT species being a chlorine radical formed *via* LMCT of excited-state iron(III) chloride.^{26a} In 2024, Lu and colleagues achieved a series of inert alkane borylations using photo-electrochemical synergistic catalysis, avoiding the use of stoichiometric oxidants;^{32a} Meanwhile, the Ackermann group also reported similar reactions, differing in cathode selection, solvent, and electrolyte, with the rest being consistent (Scheme 3).^{32b}

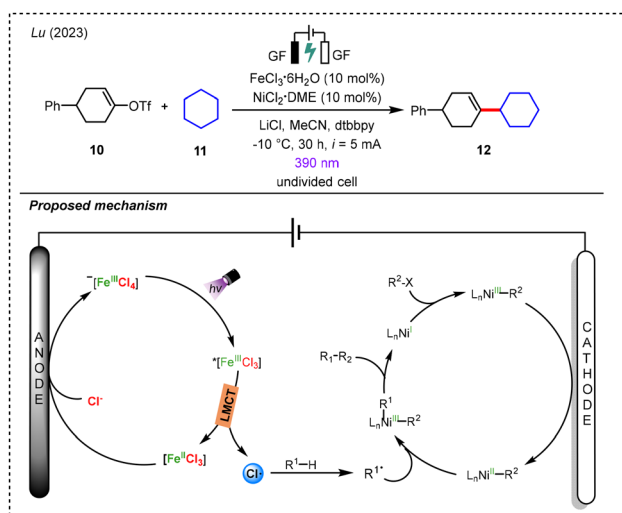
Nickel-catalyzed organic reactions have attracted attention due to their unique chemical properties, expanding many meaningful synthetic transformations such as cross-coupling, carbon–carbon bond cleavage, and directed C–H functionalization.³³ Meanwhile, the combination of photooxidation-reduction with nickel catalysis has made tremendous progress, providing pathways for the direct synthesis of target pharmaceutical organic molecules.³⁴ It is worth noting that recently, the Lu research group, along with Ackermann and Wang *et al.*,



Scheme 3 Photo-electrochemically driven iron-catalyzed C(sp³)-H arylation of alkanes.

have successfully introduced nickel into the field of photo-electrochemistry with iron, achieving bimetallic iron-nickel catalytic cycles.³⁵

In 2023, the research group led by Lu reported a novel photo-electrochemical dual catalytic strategy for the synthesis of alkene derivatives from inert alkanes and alkenyl trifluoromethanesulfonates, as illustrated in Scheme 4.^{35a} Under visible light irradiation, the excited state [Fe^{III}Cl₄] intermediate undergoes ligand-to-metal charge transfer, generating electron-affinitive chlorine radicals. These chlorine radicals abstract hydrogen atoms from alkyl groups, generating alkyl radicals, while [Fe^{II}Cl₃] is oxidized to [Fe^{III}Cl₃] at the anode. Simultaneously, Ni^{III} is reduced to Ni^I species at the cathode. The Ni^I species undergo oxidative addition with the alkene electron acceptor to form alkene-Ni^{III} intermediates, which are subsequently electrochemically reduced to alkene-Ni^{II} intermediates. Subsequently, these intermediates couple with alkyl radicals to form high-valent Ni^{III}-alkene and alkyl intermedi-

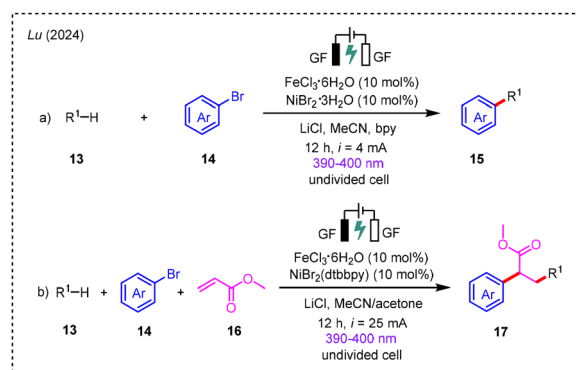


Scheme 4 C(sp³)-C(sp²) bond construction using both light and electricity.

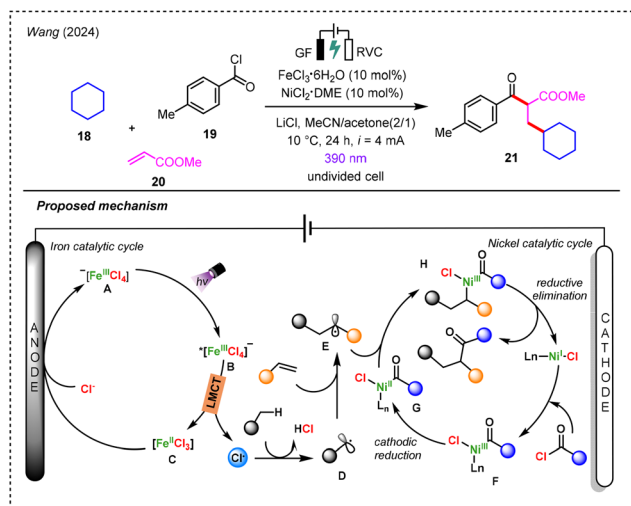
ates. Finally, the target products are generated *via* reductive elimination reactions, while the Ni^I catalyst undergoes regeneration. This reaction employs abundant crustal iron and nickel as anode and cathode catalysts, respectively. Commercially available alkene electron acceptors afford structurally diverse alkenes, including challenging all-carbon tetrasubstituted alkenes.

In recent times, Lu and colleagues have employed bi-metallic iron-nickel catalysis for the selective C(sp³)-H arylation/alkylation of alkanes, building upon their previous work. By adjusting the applied current and light source, they have successfully modulated the selectivity between two-component C(sp³)-H arylation and three-component C(sp³)-H alkylation reactions. Importantly, an extremely low anodic potential (~0.23 V vs. Ag/AgCl) has been applied in this scheme, allowing compatibility with a variety of functional groups (over 70 examples) and successful application to late-stage diversification of natural products and pharmaceutical derivatives (Scheme 5).^{35b}

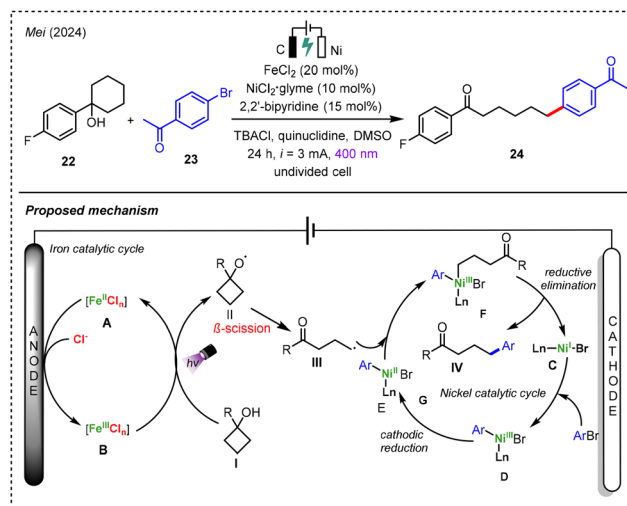
During the same period, the research group led by Wang successfully developed an iron, nickel co-catalyzed three-component carboacylation/silanoylation reaction of alkenes with acyl chlorides, hydrosilanes, and unactivated C(sp³)-H donors by combining photochemistry and electrochemistry. This electro-photocatalytic platform enables the facile construction of ketones from inexpensive commercial starting materials and exhibits excellent enantioselectivity (Scheme 6).^{35c} The possible mechanism of electro-photochemical alkene carbonylation proceeds as follows: chlorine radicals are released through the LMCT process. This highly active radical species can abstract a hydrogen atom from a C-H compound to form a carbon-centered radical intermediate **D**, while [Fe^{II}Cl₃]⁻ (**C**) undergoes anodic oxidation with chloride ions, regenerating [Fe^{III}Cl₄]⁻ (**A**). Simultaneously, Ni^I catalyst undergoes concerted oxidative addition with acyl chloride to form nickel^{III} species **F**, which is then reduced at the cathode to generate Ni^{II} species **G**. Subsequently, intermediate **D** adds to the alkene to form secondary alkyl radical **E**, which can be intercepted by Ni^{II} species **G** to form alkyl-Ni^{III} intermediate



Scheme 5 Photo-electrochemically driven selective C(sp³)-H arylation/alkylation of alkanes.



Scheme 6 Photo-electrochemical nickel-catalyzed carboacylation/silanoxylation of alkenes with unactivated C/Si-H bonds.



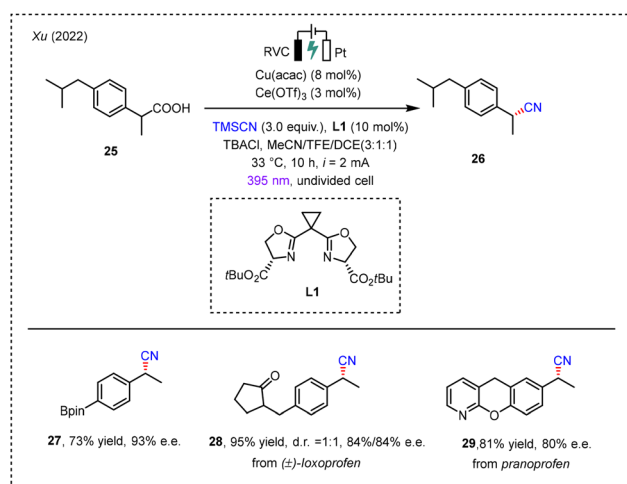
Scheme 7 Photo-electrochemical ring opening arylation of cyclic alcohols.

H. Intermediate **H** undergoes reductive elimination to yield the corresponding carbonyl compound and regenerate Ni^I catalyst.

Recently, Mei *et al.* reported a novel method that combines photo-induced LMCT catalysis with electrochemistry, using a bimetallic iron–nickel catalyst, to achieve the ring-opening arylation of cyclic alcohols.³⁶ The reaction proceeds as follows: The Ni(II) catalyst is reduced to Ni(I) species at the cathode. Through oxidative addition with an aryl bromide, with the assistance of either the cathode or another Ni(I) species, an ArNi(II)Br intermediate is formed. In the presence of anodic-generated Fe(III), the photo-induced LMCT of Fe–Cl or Fe–OR species occurs in the solution, facilitating the formation of cycloalkanoxy radicals. Subsequently, β-scission of the alkoxy radical leads to the formation of ring-opened radicals, which can be captured by the ArNi(II)Br intermediate. The Ni(III) species then undergoes rapid reductive elimination, generating the cross-coupling product and regenerating the Ni(I) species (Scheme 7).

3. Copper-catalyzed photo-electrochemical reactions

Copper-mediated cross-coupling reactions have long been recognized as efficient pathways for constructing C–C and C–heteroatom bonds.³⁷ On one hand, copper salts have gained popularity in visible-light-mediated reactions due to their low cost, high abundance, low toxicity, and intrinsic properties.³⁸ On the other hand, significant progress has been made in the study of chirally induced prochiral benzylic radicals using chiral bisoxazoline (Box)/copper catalytic systems. Building on this foundation, researchers have combined this chiral induction strategy with photochemistry, and the following is an introduction to these efforts.³⁹

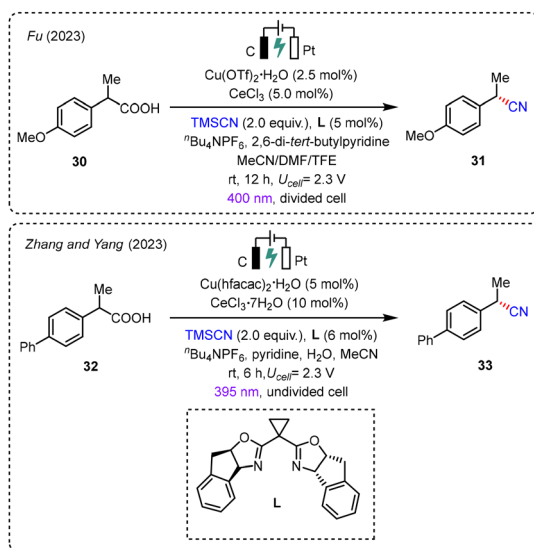


Scheme 8 Photo-electrochemical asymmetric catalysis enables direct and enantioselective decarboxylative cyanation.

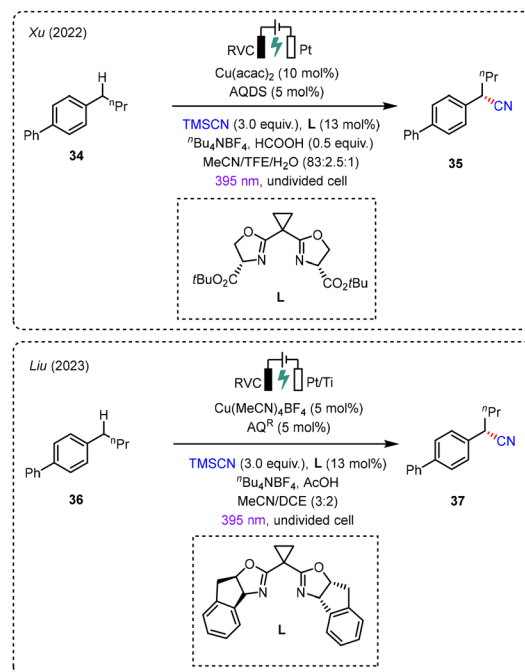
selectivity, without the need for chemical oxidants or pre-functionalization of the acid substrates, and is readily scalable.^{41a} The same year, Zhang and Yang jointly reported a copper-catalyzed selective decarboxylative cyanation protocol, achieved through the integration of photocatalysis and electrochemistry. CeCl₃ and Cu/BOX were employed as co-catalysts to facilitate the decarboxylation and cyanation reactions, with both catalysts regenerated *via* anodic oxidation^{41b} (Scheme 9).

Functionalizing ubiquitous C(sp³)-H bonds with enantioselectivity is an ideal strategy for constructing three-dimensional chiral structures. However, organic molecules often contain multiple C(sp³)-H bonds with similar energy and steric environments, making simultaneous control over site-, chemoselectivity, and stereoselectivity highly challenging.⁴² In 2022, Xu and colleagues reported the first example of photo-electrocatalytic enantioselective benzylic cyanation, demonstrating exceptional site selectivity and functional group tolerance. This reaction efficiently converts raw chemical materials and facilitates late-stage functionalization of complex bioactive molecules and natural products.^{43a} Soon after, Liu *et al.* combined electro-photochemical oxidation with copper-catalyzed enantioselective radical cyanation, developing a study on photo-electrochemical asymmetric C-H cyanation. The reaction exhibited good yields and enantioselectivity, with a broad substrate scope covering both electron-poor and electron-rich aromatic alkanes (Scheme 10).^{43b}

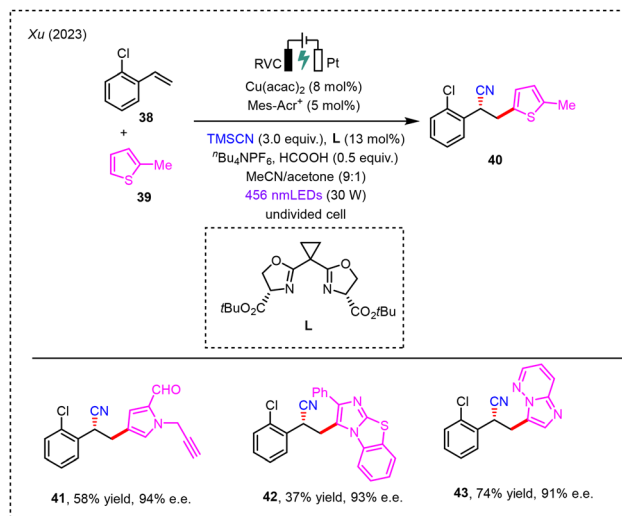
In 2023, Xu *et al.* reported a novel photo-electrochemical asymmetric catalysis method for achieving the enantioselective heteroarylcyanation of alkenes.⁴⁴ This approach utilizes unfunctionalized heteroarenes *via* C-H functionalization to transform alkenes into enantiomerically enriched compounds. By integrating photoredox catalysis and asymmetric electrocatalysis, this method facilitates the formation of two C-C bonds while circumventing the need for external chemical oxidants,



Scheme 9 Cu-catalyzed enantioselective decarboxylative cyanation *via* the synergistic merger of photo- and electro-chemistry.



Scheme 10 Photo-electrochemical asymmetric catalysis for selective benzylic C(sp³)-H bond cyanation.



Scheme 11 Photo-electrochemical asymmetric catalysis promotes enantioselective heteroarylcyanation of alkenes *via* C-H functionalization.

thus providing a new strategy for synthesizing chiral organic molecules (Scheme 11).

4. Cerium-catalyzed photo-electrochemical reactions

Exploring the potential of cerium, an abundant terrestrial element, as a photocatalyst has garnered significant attention.

Cerium, abundant in its natural resources, exhibits distinctive luminescent properties in compounds featuring both the +3 and +4 oxidation states, rendering it a promising candidate for photocatalytic applications. Utilizing cerium in photocatalysis has yielded a spectrum of reactions, encompassing decarboxylation, C–H activation, and alcohol activation, while also demonstrating promising efficacy in photovoltaic systems.^{15c} These advancements underscore the broadening scope and versatility of cerium-based photocatalytic reactions.

In 2022, the Xu research group reported an electro-photochemical method that combines organic electrochemistry with photocatalysis to achieve efficient direct decarboxylative C–H alkylation and carbamoylation of heteroaromatic compounds without the use of any chemical oxidants, enabling the effective coupling of various heteroaromatic bases with a variety of carboxylic acids and oxamic acids. Importantly, this method is scalable to decagram amounts and applicable to the late-stage functionalization of drug molecules (Scheme 12).⁴⁵

In 2022, Fu and colleagues reported an electro-photochemical dual metal-catalyzed method for the decarboxylative arylation of simple aliphatic carboxylic acids with aryl halides (Scheme 13). Cerium catalysts are responsible for decarboxylation under visible light irradiation, while nickel catalysts facilitate radical coupling. This new electro-photochemical method is mild, robust, and, most importantly, capable of

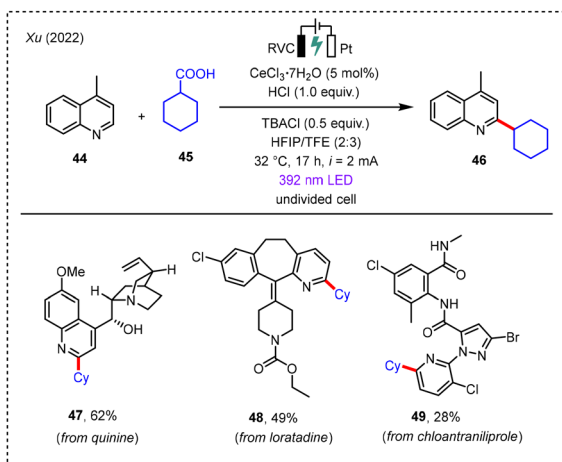
directly accommodating simple primary aliphatic acids, including acetic acid, as substrates. These acids, ubiquitous and possessing diverse structural motifs, remain challenging substrates for decarboxylative arylation.⁴⁶

Recently, Zeng *et al.* reported a ligand-to-metal charge transfer (LMCT) strategy using cerium-catalyzed electro-photo-redox reactions, enabling the incorporation of a broad range of primary, secondary, and tertiary carboxylic acids into radical cyclization cascades under external oxidant-free conditions.⁴⁷ This approach addresses the challenges associated with the synthesis of alkylated benzimidazo-fused isoquinolinones. The high functional group compatibility was demonstrated by the tolerance of ester, ketone, amide, sulfonyl, and hydroxyl groups (Scheme 14).

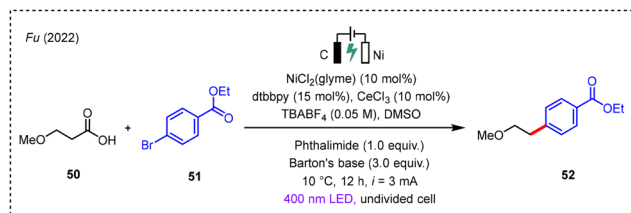
Recently, the Fu research group achieved direct decarboxylative alkenylation of widely available aliphatic carboxylic acids with vinyl halides through Ce/Ni bimetallic photo-electrocatalysis, enabling the synthesis of alkenes with various substitution patterns.⁴⁸ The reaction, which requires no external oxidants, involves oxidation cycling at the anode and cathode by cerium and nickel catalysts, respectively. This novel alkene synthesis method has been successfully applied to the direct modification of naturally occurring complex acids (Scheme 15).

In 2022, Chen *et al.* developed a novel method for the generation of Cl[•] by utilizing cerium salt as a photo-electrocatalyst in the oxydichlorination reaction of arylacetylene. This was achieved through electro-oxidation and photo-induced ligand-to-metal charge transfer. The authors conducted detailed mechanistic studies, including cyclic voltammetry, X-ray photo-electron spectroscopy, electron paramagnetic resonance, and control experiments, to elucidate the rational mechanism (Scheme 16).⁴⁹

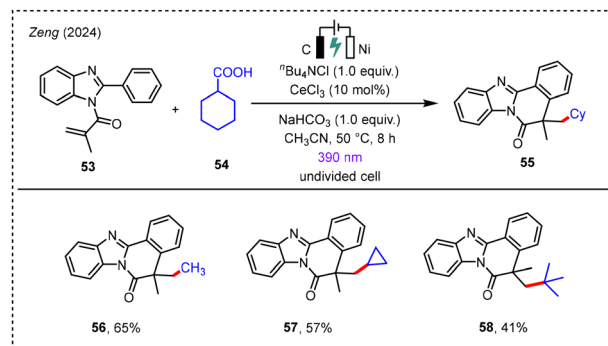
In 2022, Lei *et al.* presented a pioneering electrochemical cerium catalysis approach enabling ring-opening and ring-functionalization reactions of cyclic alcohols, encompassing cyanation, alkylation, and thioetherification reactions.⁵⁰ This methodology achieves selective cleavage of cyclopentanol of various ring sizes without the need for external oxidants under cerium catalysis, demonstrating tolerance towards multiple functional groups (Scheme 17).



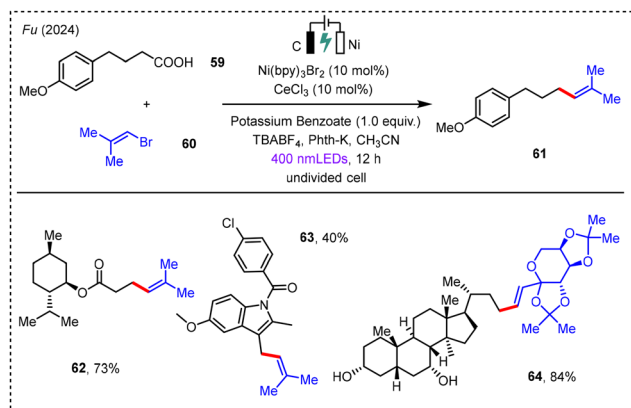
Scheme 12 Photocatalytic decarboxylative coupling of aliphatic acids via cerium-nickel bimetallic catalysis.



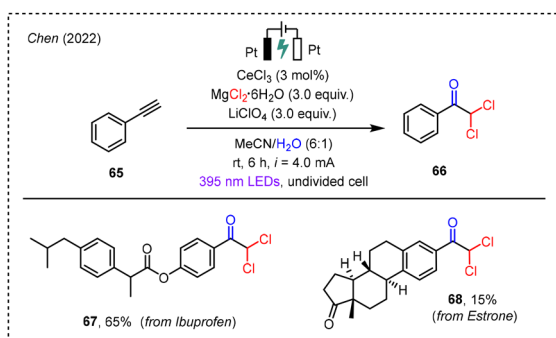
Scheme 13 Electro-photocatalytic decarboxylative C–H functionalization of heteroarenes.



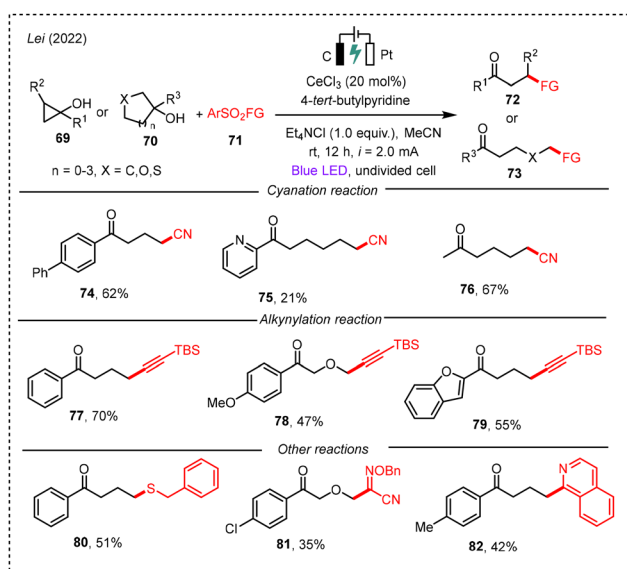
Scheme 14 Cerium-catalyzed alkylation of benzimidazo-fused isoquinolinones.



Scheme 15 Cerium-nickel bimetallic photo-electrocatalytic decarboxylative alkenylation of aliphatic carboxylic acids.



Scheme 16 Photo-electrochemical cerium-catalyzed oxydichlorination reaction of alkynes.



Scheme 17 Electro-photochemical Ce-catalyzed ring-opening functionalization of cycloalkanols.

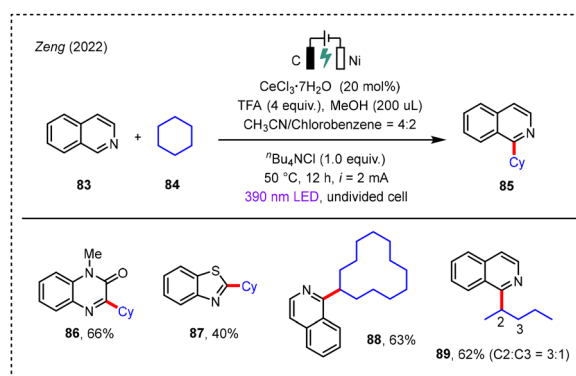
In 2022, Zeng *et al.* reported a novel electro-photocatalytic strategy for accessing alkyl radicals from strong C(sp³)-H bonds under external oxidant-free conditions, enabling the Minisci alkylation reaction.⁵¹ The interaction between cerium and alcohol, under light irradiation, generates alkoxy radicals *via* the LMCT pathway as hydrogen atom transfer (HAT) reagents, while the anode serves as an oxidant to facilitate cerium cycling and also assists in the final aromatization step of the reaction. This strategy allows for the selective conversion of abundant alkane feedstocks into value-added alkylated *N*-heteroarenes (Scheme 18).

In 2022, Zeng *et al.* reported a Ce-catalyzed photo-electrocatalytic radical addition/cyclization cascade reaction, which activates inert alkanes to synthesize alkylated benzimidazolone and other nitrogen-containing polycyclic compounds.⁵² The reaction mechanism unfolds as follows: Ce(IV) coordinates with methanol to form a MeO-Ce(IV)Cl_{n-1} complex, which, upon light exposure, undergoes a LMCT process, leading to molecular cleavage and the generation of a methoxy radical. Subsequently, a hydrogen atom abstraction (HAT) from cyclohexane produces a cyclohexyl radical (I), which then undergoes a radical addition/cyclization cascade reaction with 90 to form intermediate III. Finally, III is oxidized by Ce(IV) through a single electron transfer (SET) process, followed by deprotonation, leading to the formation of the final product 92 (Scheme 19).

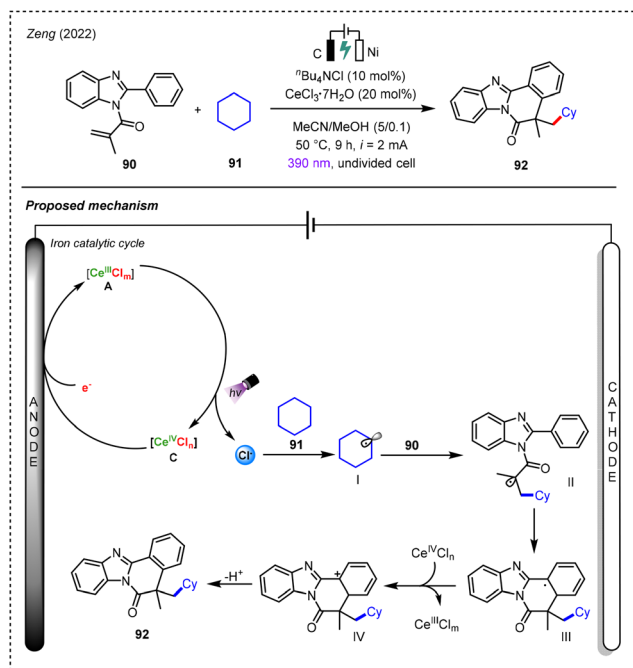
5. Other metal-catalyzed photo-electrochemical reactions

Manganese (Mn), as a non-toxic transition metal, has attracted attention in various fields such as hydrogenation, cross-coupling, and C-H activation,^{1e,53} due to its high abundance. Furthermore, significant progress has been made in manganese-catalyzed azidation reactions using TMSN₃ or NaN₃ as azide sources.⁵⁴

In 2020, Lei *et al.* reported a manganese-catalyzed method for C(sp³)-H amination using a nucleophilic NaN₃ as the diazo

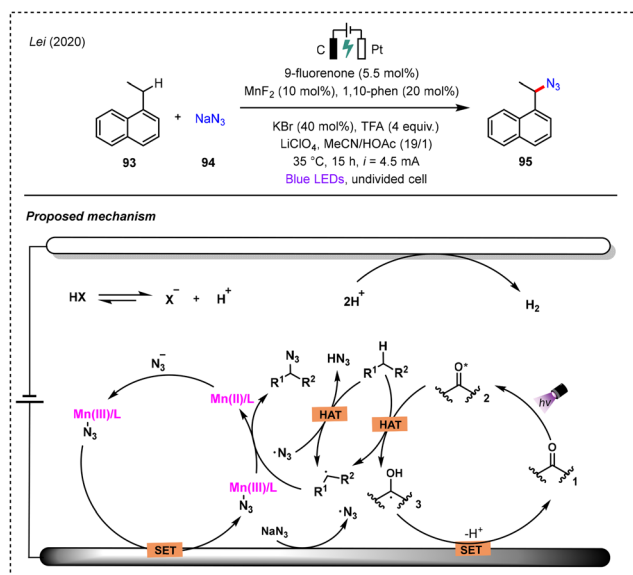


Scheme 18 Electro-photocatalytic C-H functionalization of *N*-heteroarenes with unactivated alkanes.



Scheme 19 Electro-photoredox/cerium-catalyzed activation of unactivated alkanes for the synthesis of alkylated benzimidazo-fused isoquinolines.

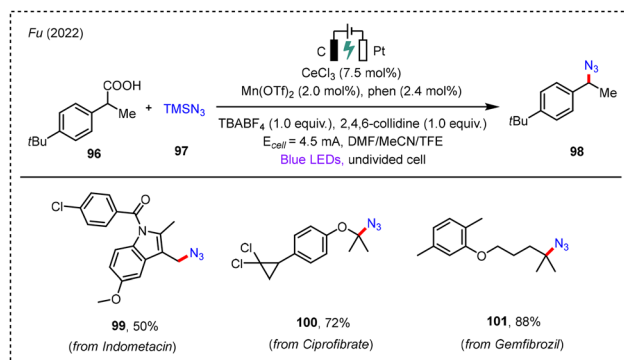
source and 9-fluorenone as the photosensitizer.⁵⁵ The reaction was carried out under photo-electrocatalytic conditions. One remarkable feature of this method is that it does not require an excess of substrates and effectively avoids the use of chemical oxidants. The reaction exhibits broad generality and can be applied to the late-stage modification of pharmaceutical molecules (Scheme 20).



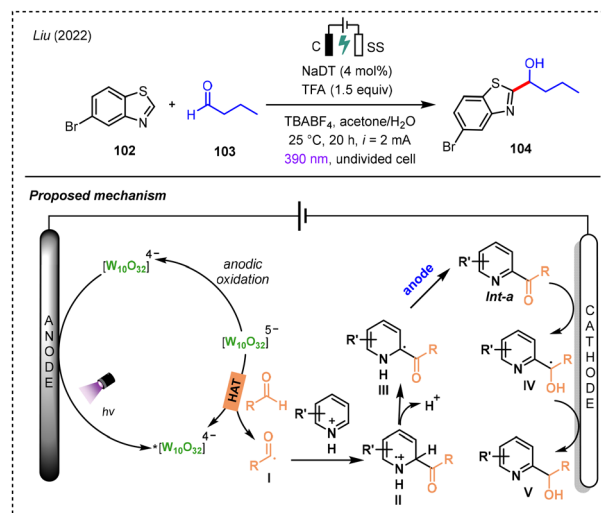
Scheme 20 Manganese-catalyzed oxidative azidation of C(sp³)-H bonds under photo-electrocatalytic conditions.

In 2022, Fu *et al.* reported a novel photo-electrochemical co-catalytic method for the decarboxylative azidation of aliphatic carboxylic acids.⁵⁶ This reaction, similar to the previous method, does not require the use of chemical oxidants or azido-group transfer reagents. It utilizes a manganese catalyst in complexation with azide anions to achieve azidation of various aliphatic carboxylic acids. Importantly, this method can also be applied for the late-stage modification of pharmaceutical molecules (Scheme 21).

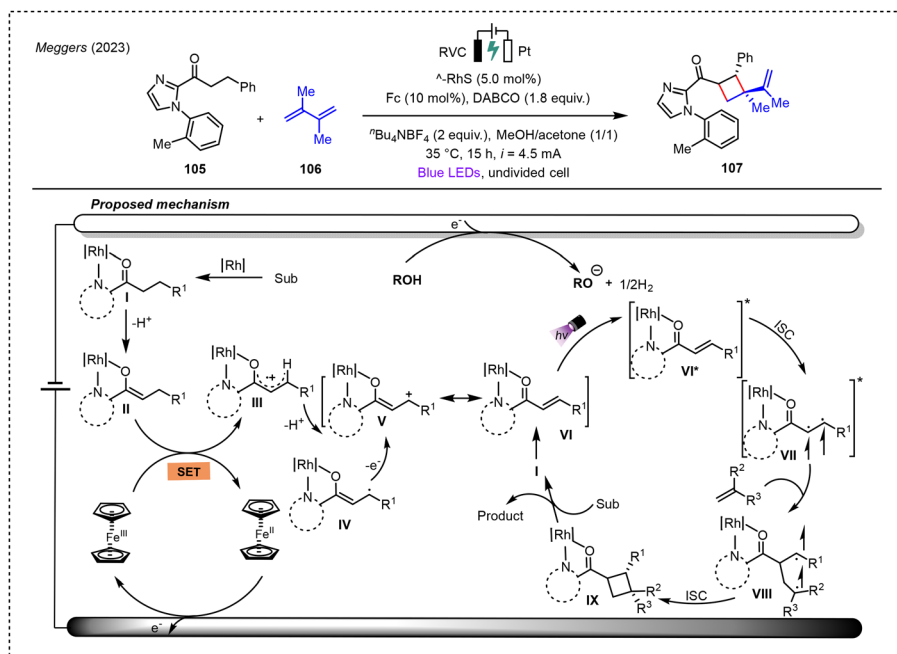
Tungsten (W) is renowned as one of the hardest metals, with a crustal abundance of 0.001%. Its primary application lies in the production of hard alloys.⁵⁷ Additionally, tungsten compounds have made notable progress in areas such as oxidative dehydrogenation coupling and borane hydride reactions.⁵⁸ However, in the field of synthesis, the decatungstate anion (W₁₀O₃₂⁴⁻) has garnered extensive research attention as a result of its unique photocatalytic properties, particularly as a reagent for hydrogen atom transfer (HAT) reactions.⁵⁹



Scheme 21 Electro-photochemical decarboxylative azidation of aliphatic carboxylic acids.



Scheme 22 Electro-photocatalytic C-H hydroxyalkylation of heteroaromatics with aldehydes.



Scheme 23 Photo-electrochemical asymmetric dehydrogenative [2 + 2] cycloaddition between C–C single and double bonds via the activation of two C(sp³)–H bonds (this is a double-column scheme).

In 2022, Liu *et al.* introduced a groundbreaking application of decatungstate in a photo-electrochemical system, leading to the development of a novel method for the electro-photo-catalytic C–H hydroxyalkylation of *N*-heteroaromatics with aldehydes. The decatungstate anion exhibited remarkable versatility in this transformation, serving as a multifaceted catalyst with roles encompassing photocatalysis, electrocatalysis, and hydrogen atom transfer. By directly harnessing the energy from the aldehyde's C–H bond, the generation of acyl radicals was facilitated, effectively initiating the Minisci-type C–H functionalization reaction. The exceptional atom economy and gentle photo-electrocatalytic properties of this approach position it as an alternative and particularly challenging method for the hydroxyalkylation of *N*-heteroaromatics, enabling the efficient synthesis of secondary alcohols using readily available starting materials (Scheme 22).⁶⁰

In 2023, Meggers and colleagues reported a novel synthesis method that combines photo-electrochemistry with asymmetric catalysis to achieve enantioselective dehydrogenative [2 + 2] photocycloaddition between alkyl ketones and alkenes under rhodium (Rh) catalysis.⁶¹ This method eliminates the need for chemical oxidants and successfully synthesizes structurally complex chiral cyclobutanes, including all-carbon quaternary stereocentres, through the reaction of C–C single bonds with C=C double bonds. By simultaneously activating two C(sp³)–H bonds and two C(sp²) carbons, it enables the construction of up to four consecutive stereocentres with excellent enantioselectivity and broad substrate compatibility. The key to the success of this reaction lies in the utilization of ferrocene as a redox mediator, promoting the formation of a

homogeneous electrocatalytic system. Furthermore, this methodology demonstrates its practical value by enabling the synthesis of chiral natural product melicoptine C through photo-electrocatalysis (Scheme 23).

6. Conclusions

In this review article, we have focused on the recent developments of photo-/electro-chemically promoted organic synthetic reactions, with a particular emphasis on metal-catalyzed transformations. The metals involved mainly include iron, copper, cerium, manganese, nickel, *etc.* Nowadays, the role of metals in organic synthesis has been increasingly explored, ranging from thermal reactions to synergistic catalysis with traditional photosensitizers and integration with electrochemistry. Moreover, metals have been introduced into the currently popular photo-electrochemical systems, showcasing their immense potential. The combination of light and electricity not only ensures mild reaction conditions but also avoids the use of stoichiometric oxidants and reductants, thereby maximizing the activity of metal catalysts. These reactions have demonstrated remarkable performance in C–H activation, decarboxylation, alcohol activation, and cross-coupling. However, it should be noted that the current repertoire of metal catalysts in photo-electrochemical systems is still limited, and certain reaction types are still constrained. Future research should focus on expanding the variety of metal catalysts to overcome the limitations of traditional chemistry and enable transformations that were previously challenging to achieve. This will

further broaden the applications of photo-electrocatalysis, providing numerous opportunities and possibilities for future advancements.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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