Science for Energy and Environment

Review

Research Progress in Photocatalytic Organic Transformation: From Materials to Applications

Chuanzhe Wang [1], Junshan Li [2], and Yongfa Zhu [1,*]

[1] Department of Chemistry, Tsinghua University, Beijing100084, China
[2] Institute for Advanced Study, Chengdu University, Chengdu 610106, China
* Correspondence: zhuyf@mail.tsinghua.edu.cn

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Abstract: Photocatalytic organic transformation, as a mild, green, and environmentally friendly synthesis method, has attracted increasing attention as a sustainable development scheme to address the global energy crisis and environmental problems. At present, a variety of materials have been used to develop various photocatalytic organic conversion reactions. The development of high-efficiency photocatalytic materials, which necessitates a comprehensive understanding of their catalytic mechanisms, is essential to enhancing the performance of photocatalytic organic transformation. However, only a few studies summarize and discuss the results of research on materials and mechanisms involved in photocatalytic organic transformation. In this review, we aim to cover the development of photocatalysts, including metal and its oxide materials, organic semiconductors, metal-organic frameworks, covalent-organic frameworks, and other materials. Then, the general mechanisms, unique advantages, and strategies in photocatalysis synthesis are discussed. In addition, it also provides an overview of applications in various organic reactions, such as oxidation, reduction, coupling, cyclization, and asymmetric synthesis. Finally, we summarize the challenges and prospects of material design and reaction mechanisms in photocatalytic organic synthesis in the future.

Keywords: organic transformation; photocatalysis; active species

1. Introduction

Organic transformations are essential and ubiquitous in contemporary chemical and pharmaceutical synthesis [1,2]. They play a crucial role in advancing human society and driving innovations in a wide range of industries, including pharmaceuticals, agriculture, energy, and materials science. Over the years, organic transformations have become central to the advancement of synthetic chemistry, offering new avenues for the creation of valuable compounds with diverse applications in medicine, agriculture, and industrial processes [3–5]. However, traditional organic transformation processes not only require significant amounts of fossil energy but also generate pollutants, leading to a severe energy crisis and exacerbating environmental issues. To address the above problems, it is necessary to search for new clean energy sources to meet the needs of the sustainable development of human society. Harnessing sustainable solar energy to realize organic transformations by photocatalysis has the merits of easy manipulation, environment consistency, and recyclability [6,7]. Thus, it offers an economically and environmentally attractive pathway to generate energetic electrons and holes to trigger transformations.

Photocatalytic organic synthesis has emerged as a transformative approach in the field of green chemistry, offering a sustainable and efficient way to carry out chemical reactions under mild conditions. By harnessing the energy of light, photocatalysis enables the activation of chemical bonds and the formation of highly selective products with minimal energy consumption and reduced environmental impact [8–10]. This approach has attracted significant attention due to its ability to replace traditional methods that often rely on toxic reagents, high temperatures, or pressure [11]. As for photocatalytic organic transformations, the conversion efficiency and selectivity are two momentous indicators. The conversion efficiency mainly depends on light capture, charge separation, and redox reaction, and the selectivity mainly lies in band gap, composite, morphology, and surface effect [12,13]. Photosensitizers of homogeneous photocatalytic systems based on transition metal complexes or precious metal complexes have achieved significant breakthroughs in the field of organic transformations. Studies have demonstrated that these homogeneous photocatalysts exhibit exceptional catalytic activity in various chemical reactions [14]. While these homogeneous photocatalysts demonstrate superior catalytic activity in various chemical reactions, they face limitations such as relatively high synthesis costs and difficulties in efficient recovery, which hinder their application [15,16]. On the contrary, heterogeneous photocatalysts offer promising alternatives owing to their excellent durability and recyclability. A large number of studies have demonstrated that tailoring the band structures of semiconductors or developing composite materials (S-scheme or Z-scheme heterojunctions) effectively improves charge separation and transfer efficiency in photocatalytic organic transformations [17–19]. Currently, heterogeneous catalytic materials suffer from several limitations, including narrow light absorption range, susceptibility to photodegradation, poor durability, complex structural modifications, and high rates of photogenerated carrier recombination. These drawbacks result in suboptimal performance in photocatalytic applications, developing photocatalysts with well-defined structural features remains particularly appealing [20,21]. This approach facilitates the elucidation of structure-activity relationships and serves as a foundation to guide the rational design of next-generation photocatalysts with enhanced performance.

At present, a diverse array of organic and inorganic heterogeneous photocatalysts has been developed, including metal oxides and sulfides [22], carbon nitrides [23], covalent organic frameworks [24], and metal-organic frameworks [25]. These photocatalysts have been applied to a variety of organic reactions as shown in Figure 1. However, their large-scale application is severely hindered by their low quantum efficiency. Therefore, the development of efficient photocatalysts is essential for advancing the industrialization of photocatalysis. This review provides an overview of the current research field of photocatalytic organic synthesis, types of photocatalysts, mechanisms and active species of photocatalytic synthesis, Subsequently, various organic transformations, including oxidation, reduction, coupling, cyclization and cycloaddition, and asymmetric reactions over photocatalysts are introduced, and a detailed discussion of important organic synthesis reactions.

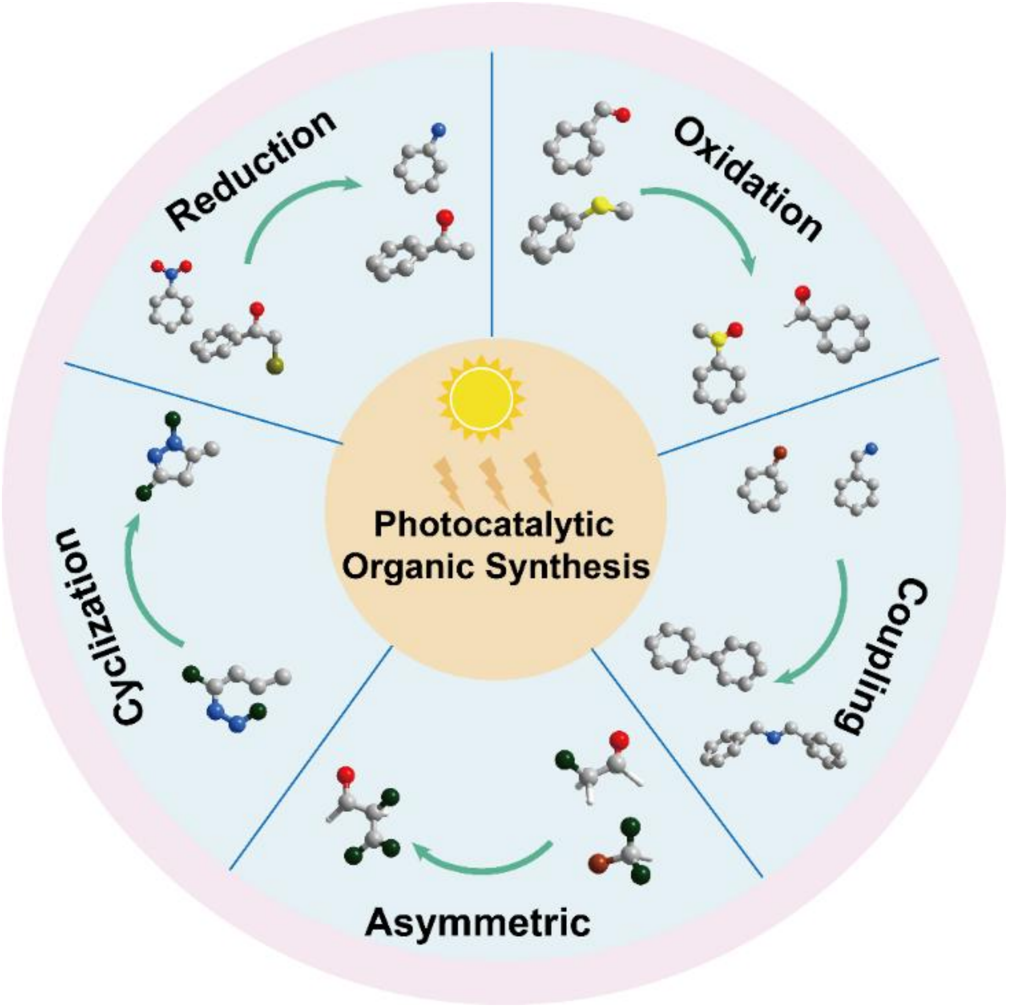

Figure 1. Schematic illustration of photocatalytic organic synthesis.

2. Basic Principles and Characteristics

Typical photocatalytic organic transformations are generally triggered by the photocatalysts absorbing photons. Typically, a series of photophysical/photochemical processes are involved in the photocatalytic reactions: (i) Light-harvesting; (ii) Photogeneration and separation of the electron–hole pairs; (iii) Migration of the photogenerated electrons and holes to the catalyst surface; (iv) Surface redox reactions induced by the photogenerated electron (e−) and hole (h+) [26–28]. When the energy of photons is equal to or greater than the band gap (Eg) of the photocatalysts, the electrons will be excited from the valence band (VB the highest energy band occupied by electrons) of the photocatalyst to the conduction band (CB the lowest energy band without electrons), resulting in the generation of electron-hole pairs [29,30]. After these electron-hole pairs migrate to the photocatalyst surface and interact with target molecules. Electrons will react with acceptors, giving reduction products, while holes can react with donor species to generate oxidation products. This interplay between electrons and holes with acceptors and donors results in the formation of reduction and oxidation products, respectively. On the other hand, electron-hole pairs can react with water, oxygen or substrates to produce free radicals, which trigger the radical mechanism. The efficiency of these processes can be influenced by factors such as recombination rates and the specific chemistry of the photocatalyst and reactants involved.

Conventional chemical routes for organic transformations generally require harsh operating conditions such as high temperatures and high pressures. Photocatalytic organic transformations offer a viable alternative, which is characterized by mild reaction conditions and high selectivity. The research on the application of photocatalysis in organic synthesis focuses on the mechanism. This reaction usually includes photocatalytic activation of small molecules as the main photocatalytic step. Photocatalytic organic synthesis methods are mainly classified into three categories, including (i) reactions of organic substrates with photocatalytically activated small molecules, (ii) a direct photocatalytic activation of one organic substrate, and (iii) reactions involving a direct activation of two organic molecules (Figure 2) [31,32]. This classification covers all main types of transformations of organic molecules oxidation, reduction and coupling.

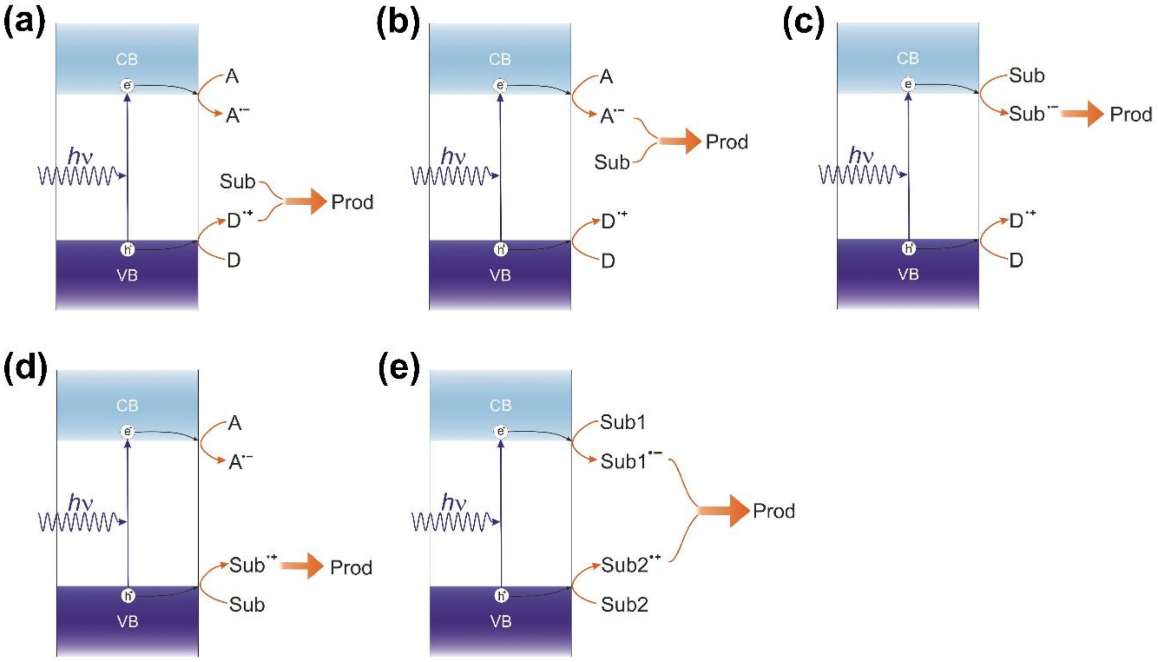

Figure 2. Classification of photocatalytic transformations of organic compounds (substrates to products): (**a**,**b**) reactions initiated by the reduction and oxidation of two small molecules (acceptor A, donor D); (**c**,**d**) reactions initiated by a direct reduction or oxidation of an organic substrate (Sub); (**e**) reaction involving direct reduction and oxidation of organic substrates (Sub1, Sub2) [31]. Copyright © 2024 Wiley-VCH GmbH.

3. Reaction Types of Photocatalytic Organic Synthesis

3.1. Oxidation Reaction

The remarkable capacity of photocatalysts and visible light-driven photocatalysts to realize organic synthesis through sophisticated oxidation processes has garnered significant interest, and emerged as a significant area of research in green chemistry, attracting increasing attention in recent years. The reactions typically occur under mild conditions without the need for toxic oxidants or high-temperature, high-pressure equipment. Numerous types of photocatalytic oxidation reactions include the oxidation of aromatic compounds [33], oxidation of secondary amines [34], oxidation of sulfides [35], and oxidation of alcohols [36], which not only provide efficient routes for synthesizing valuable chemicals but also contribute to reducing environmental pollution and advancing sustainable development.

A significant portion of the documented photocatalytic organic transformations involves photochemical oxidation reactions, in which O_2^- and $^1O_2$ are the primary reactive oxygen species [37–39]. In addition, the •OH and H_2O_2 converted by direct or indirect means from water or oxygen sometimes also play an important role in the reaction.

3.2. Reduction Reaction

Reductive organic transformations play a pivotal role in both academic research and industrial applications for the synthesis of valuable chemical compounds [40–42]. Despite significant advancements, the reductive conversion of inert substrates remains a challenging study area. Current methodologies often involve the use of strong reducing agents in excess quantities, UV light irradiation, which give rise to issues such as high costs and potential safety hazards [43–45]. Photocatalytic reduction represents a significant category of light-driven organic transformations. The main photocatalytic reduction reactions include reductive dehalogenation of halogenated ketones [46], reduction of aromatic nitro compounds [47], and selective hydrogenation of unsaturated C=C and C=O double bonds [48].

3.3. Coupling

The construction of C-C and C-N bond is one of the cores of chemistry and an important basis for synthetic chemistry, pharmaceutical engineering, natural product synthesis and material science and technology. At present, the coupling reaction has been successfully used for the efficient construction of C-C or C-N bonds and has been widely used in the fields of chemistry, chemical industry and medicine [49–51]. Photocatalytic C-C or C-N coupling reactions avoid the extensive use of homogeneous catalysts, especially precious metal catalysts, and meet the needs of sustainable development [52,53]. To establish this type of reaction, it is also necessary to use a nucleophile precursor carbon center. Unlike the traditional transition metal catalysis process, the carbon nucleophile precursor does not need to be converted into a highly alkaline carbon anion species. Generally, an alkyl radical intermediate is formed through single electron transfer or hydrogen atom transfer under the action of a photocatalytic catalyst, and then combined with other species to achieve coupling with a carbon electrophile [54,55]. The reaction system is significantly milder, which enhances the applicability of the substrate and overcomes the limitations of conventional systems.

3.4. Cyclization and Cycloaddition

Cyclization and cycloaddition reactions are common methods for constructing cyclic skeletons in an environmentally friendly manner. While traditional photochemical approaches have conventionally relied on high-energy UV irradiation, recent advancements in photocatalytic have brought about groundbreaking progress in this field [56–58]. In recent years, the visible-light-mediated photocatalytic cycloaddition reaction has garnered significant attention and achieved remarkable progress in this field. The photocatalytic system is no longer limited to the ultraviolet light, instead, blue light or even milder green light can effectively facilitate these reactions. Furthermore, the substrate scope for cycloaddition reactions has been greatly expanded. For instance, both electron-rich and electron-deficient substrates can undergo photocatalytic cyclization via single-electron transfer, achieving photoreduction and photooxidation. Additionally, photocatalytic mediated cycloadditions through energy transfer have further broadened the scope [59]. However, visible-light-mediated photocatalytic for constructing complex cyclic frameworks or pharmaceuticals remains relatively underexploited. Moreover, developing highly efficient transformations for large-scale photocatalytic cycloaddition reactions should be a long-term goal in this field to achieve environmental and resource benefits.

3.5. Asymmetric Reactions

Asymmetric photocatalysis plays an important role in organic synthesis. The delicate combination of photosensitizers and asymmetric catalysts can achieve stereoselective photocatalysis. Asymmetric organic synthesis can effectively promote asymmetric transformation of isomers due to its unique size and spatial effects, and exhibits excellent yield and enantioselectivity in asymmetric alkylation reactions. This places very high demands on the structural design of the catalyst, which requires a chiral active center [60,61].

4. Types of Photocatalyst

4.1. Inorganic Semiconductors

Due to their distinctive electronic properties, inorganic semiconductors have emerged as highly promising candidates for light absorption in artificial photosynthesis systems. Their forbidden energy gap (commonly referred to as bandgap) exhibits a unique advantage: It corresponds to the energy range of near-ultraviolet (UV) and visible light, making them particularly suitable for harnessing solar energy in photosynthetic applications. Titanium dioxide is the most widely studied inorganic semiconductor material [62]. Although the large bandgap semiconductor requires UV light irradiation to form electron-hole pairs, it is among the most frequently applied heterogeneous photocatalysts in organic synthesis. The most recent research found that TiO_2 also performed well as a photocatalyst under visible light irradiation. For instance, Wang et al. [63]. demonstrate that introducing abundant oxygen vacancies on the surface of titanium dioxide (TiO_2) facilitates the activation of O_2 through a two-electron reduction process instead of a single-electron reduction, thus effectively suppressing the generation of $O_2^{\bullet-}$ during the photocatalytic oxidation of benzene with O_2 (Figure 3a). This effectively improves the selectivity of aerobic oxidation of benzene to phenol. Rueping et al. [64]. reported an environmental friendly, direct arylation of heteroarenes using an easily accessible, cheap and recyclable TiO_2 heterogeneous catalyst (Figure 3b). The catalyst is applied in the arylation of electron-rich and-poor heteroarenes delivering the products in moderate to excellent yields. Furthermore, except for furan and thiophene, pyridine could also be applied in such reactions.

To enhance photocatalytic efficiency and expand its practical applications, extensive research efforts have been dedicated to systematically investigating structural regulation strategies for inorganic semiconductor materials. These strategies include optimizing microstructures, constructing composites with other functional materials, and designing specific nano configurations [65]. Exploring advanced two-dimensional (2D) photocatalysts by introducing surface defects, hybrid structure, and structural distortions are demonstrated to be effective strategies for increasing conversion efficiency and selectivity of relevant photocatalytic reactions. Xiong et al. [66]. reported the defects on WO_3 nanosheets with numerous surface coordinately unsaturated sites on surface for oxygen activation (Figure 3c). This mechanism facilitates the generation of chemisorbed superoxide radicals ($O_2^{\bullet-}$), which subsequently interact with neighboring adsorbed amine molecules. By effectively harnessing broadband solar energy, this strategy enables the efficient aerobic coupling of amines to their corresponding imines, achieving remarkable improvement in reaction kinetics. Compared to defect-deficient WO_3, the system demonstrates a 6-fold enhancement in reaction rate. In another case, Loh et al. [67]. reported that porous 2D-CdSe photocatalyst is used to a universal C-X to C-D transformation using D_2O as deuterium source. A wide range of organic iodides including aryl-, alkyl-, and alkynyl iodides can be effectively deuterated in excellent yields and with good functional groups tolerance (Figure 3d).

Perovskite-based photocatalysts have emerged as an application platform in photocatalytic organic synthesis due to their distinctive physicochemical characteristics. These materials exhibit exceptional light-harvesting capabilities across a broad spectrum, prolonged excited state lifetimes, and outstanding photoluminescence quantum efficiencies. Furthermore, their superior ability to facilitate charge carrier separation and migration has positioned them as highly efficient candidates for driving photocatalytic organic transformations. Yan et al. [68]. prepared the perovskite nanocrystals for organic reactions of C-C bond formations via C-H activation, C-N, and C-O formations via N-heterocyclizations and aryl-esterifications can be achieved with moderate to high yields (Figure 3e).

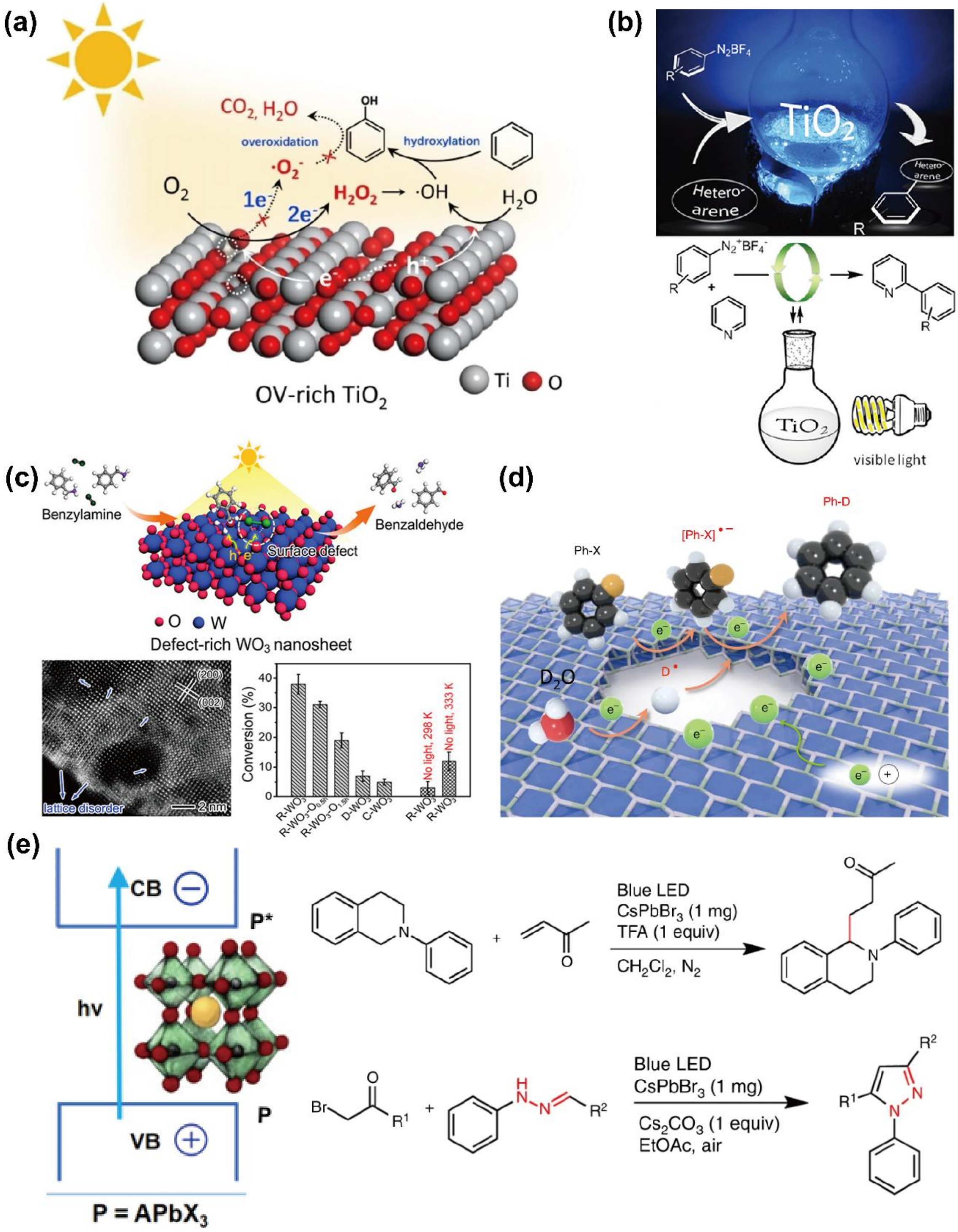

Figure 3. (**a**) Photocatalytic oxidation of benzene to phenol in OV-rich TiO_2 [63]. Copyright © 2025 Wiley-VCH GmbH. (**b**) C-H arylation of heteroarenes catalyzed by TiO_2 under visible light irradiation [64]. Copyright © 2015 American Chemical Society. (**c**) Defected-rich WO_3 nanosheets drive benzylamine to benzaldehyde [66]. Copyright © 2016 American Chemical Society. (**d**) Possible radical pathway for C-X to C-D transformation in porous 2D-CdSe photocatalyst [67]. Copyright © 2018 Springer Nature. (**e**) $CsPbBr_3$ perovskites for C-C and C-N bond formation reactions [68]. Copyright © 2019 Springer Nature.

4.2. Organic Semiconductors

Organic semiconductors, composed primarily of carbon, hydrogen, oxygen, and nitrogen compounds, represent a unique class of semiconducting materials. Their inherent structural flexibility allows for precise modification of optical and electronic properties, including absorption spectra and photoelectric characteristics. This tunability makes them particularly valuable in photocatalytic applications, where their properties can be optimized to significantly improve the efficiency of organic synthesis processes. The primary advantage of organic semiconductors stems from their remarkable structural adaptability, which allows for precise adjustments to their chemical and crystalline configurations, facilitating significant improvements in photocatalytic activity [69,70].

Organic semiconductor materials are both photo- and chemically stable, and feature an appropriate bandgap between the valence band maximum and conduction band minimum, allowing for the controlled oxidation and reduction of various practical substrates. König et al. [71]. reported organic semiconductor mesoporous graphitic carbon nitride (mpg-CN) as a heterogeneous photoredox catalyst for synthetically important functionalizations of arenes and heteroarenes. By using alkyl bromides as the source of two different functional groups, mpg-CN photocatalytic has achieved arene $C(sp^2)$–$C(sp^3)$/$C(sp^2)$-heteroatom bifunctionalizations at two distinct sites (Figure 4a). The mpg-CN, upon photoexcitation, naturally generates electron and hole pairs, and its stability and associated electron-hole transfer kinetics enable easy execution. Furthermore, the researcher developed direct C-H monofunctionalizations of arenes and heteroarenes by mpg-CN.

Small-molecule organic semiconductors have been used in a vast number of photoelectronic applications, owing to unique optical and electronic properties originating. Zhang et al. [72]. reported a series of new metal-free visible-light-active photocatalysts with tunable absorption regions and defined band structures based on structural design principle of electron -donor and -acceptor. The catalyst realized intermolecular C-H functionalization of electron-rich heteroaromates with malonates with the highest yield of 86% (Figure 4b). In addition, one of the organic semiconductors perylene diimide supramolecular (PDIs) materials have been extensively studied and applied in photocatalytic owing to their moderate bandgap, high molar extinction coefficient, abundant element resources, excellent photothermal stability, and easy preparation. For example, Zhu et al. [73]. prepared an ultrathin porous PDI photocatalyst with photooxidation abilities for the oxidation reaction of 1,2,3,4-tetrahydroisoquinoline (THIQ) to 3,4-dihydroisoquinoline (DHIQ). After irradiation for 15 h, the conversion rate of triphenylamine PDIs reached 90%, with a selectivity of 92% and 84% yield. Notably, the yields of other N-heterocyclic substrate, such as indoline and tetrahydroquinoxaline, were all greater than 90% (Figure 4c). This work offers viable strategies and promising avenues and advances the field of photocatalytic selective oxidation technology.

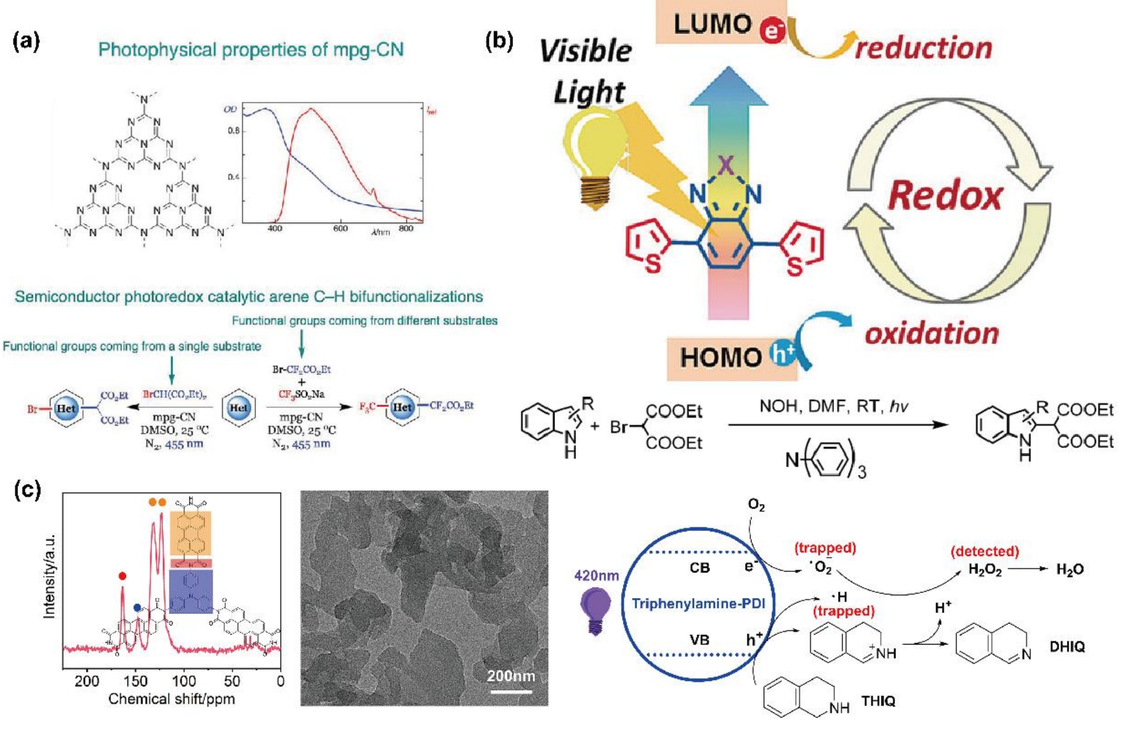

Figure 4. (**a**) Relative band positions and redox potentials and photocatalytic performance of mpg-CN [71]. Copyright © 2019 Science. (**b**) Reaction mechanism of the intermolecular C-H functionalization of small-molecule organic semiconductors [72]. Copyright © 2016 Wiley-VCH GmbH. (**c**) Solid-state ^{13}C-NMR spectra and TEM image and reaction mechanism for photocatalytic oxidation of THIQ to DHIQ [73]. Copyright © 2022 Wiley-VCH GmbH.

4.3. Metal-Organic Frameworks

Metal-organic frameworks (MOFs) have unique structural advantages, such as high specific surface area, porosity, structural tunability, and functionalization, which have become important research objects in the field of photocatalysis [74]. The research based on semiconductor photocatalysis focuses on the conversion of small molecules such as hydrogen production and CO_2 reduction. With the continuous pursuit of production value, researchers are paying more and more attention to light-induced organic conversion reactions. The types of photocatalytic organic conversion include: (1) oxidation of olefins, alkanes and sulfides; (2) Dehalogenation of aromatic compounds; (3) C-H activation; (4) Oxidation of amines, etc. Jiang et al. [75]. designed and synthesized Pt/PCN-224(M) composites by combining Pt nanocrystals with porphyrin MOFs materials PCN-224(M). Based on the synergistic photothermal effect and the generation of singlet oxygen, the selective photocatalytic oxidation of benzyl alcohol in 1 atm O_2 at room temperature was improved (Figure 5a). C-C bond coupling usually requires the participation of some noble metals. The direct formation of new C-C bonds from low-reactivity sp^3 C-H bonds through photocatalytic oxidation coupling avoids noble metals and complex reaction systems. Photocatalytic C-C or C-N coupling reaction by MOFs avoid the extensive use of homogeneous catalysts, especially noble-metal catalysts, which is in line with the need for sustainable development. Duan et al. [76]. reported through careful incorporation of both bis(3,5-dicarboxyphenyl)pyridine and bis(3,5-dicarboxyphenyl)-methylpyridinium ligands into a single MOF, developed a promising two-photon responsive photocatalytic path to realize photocatalytic C-N and C-C oxidative coupling reactions (Figure 5b). In addition, photon intensity dependent studies exhibit a nonlinear correlation between catalytic efficiency and photon power intensity, demonstrating that the two-photon process facilitates accumulation of sufficient energy for the visible-light-driven photocatalytic reactions.

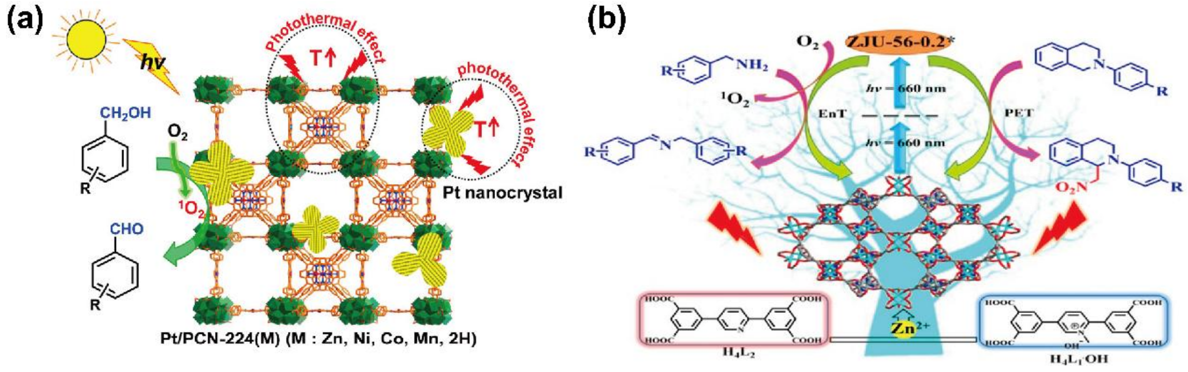

Figure 5. (**a**) The singlet oxygen-engaged selective oxidation of alcohols over Pt/PCN-224(M) [75]. Copyright © 2017 American Chemical Society. (**b**) Representation of the ZJU-56 for the coupling reactions of benzylamine or N-phenyltetrahydroisoquinoline [76]. Copyright © 2018 American Chemical Society.

4.4. Covalent Organic Frameworks

Covalent organic frameworks (COFs) are a new class of porous crystalline materials connected by strong covalent bonds. These materials feature ordered characteristics of excellent porosity, high surface area, and superior thermo-chemical stability. These characteristics enable COFs to serve as bifunctional materials, possessing both adsorption and catalytic properties, which makes them highly effective as materials [77,78]. In recent years, COFs have attracted great interest as efficient and environmentally friendly photocatalytic materials. Due to their distinct properties, including high charge carrier mobility and efficient charge separation, COFs have become prominent photocatalysts in various chemical reactions. Meanwhile, in the realm of photocatalysis for organic transformation, predominant synthetic approaches, including the bottom-up synthesis strategy, the post-modification approach, and the hybrid strategy, are currently employed to enhance the photocatalytic efficiency of organic reactions to different degrees. Liu et al. [79]. have reported a novel stable amide-linked 2D-COF, denoted as COF-JLU5, that features permanent porosity, high surface area, large pore volume, high crystallinity and stability. COF-JLU5 was synthesized under solvothermal conditions by condensation of 1,3,5-tris-(4-aminophenyl)triazine. In this work, the COF-JLU5 can catalyze oxidative C-H functionalizations reaction in N-arylte-trahydroisoquinolines under visible-light and exhibits high catalytic activity, broad substrate adaptability and outstanding recyclability. Under the optimized conditions, the conversion of N-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane using COF-JLU5 was up to 99% (Figure 6a).

The recent breakthroughs in material of COF design have played a crucial role in driving the advancement of photocatalytic. Many researchers have successfully incorporated novel functionalities into COFs through post-modification synthesis, yielding functionalized frameworks endowed with diverse properties tailored for a broad spectrum of applications. In 2021, Mas-Ballesté et al. [80]. embedded Ir and Ni metal complexes into phenanthroline units within a novel imine-based Phen-COF (Figure 6b). This innovative design facilitated the synergistic interaction between the two catalytic metal centers, thereby enabling the efficient formation of Csp^3-Csp^2 bonds. The photocatalytic performance of obtained Ir,Ni@Phen-COF was evaluated in the cross-coupling reaction of aryl bromides with diverse radical precursors, including N-protected proline, organic silicates, and potassium benzyl and alkoxy-trifluoroborates. Under optimized reaction conditions, the catalyst demonstrated excellent performance, achieving high yields for the desired products.

The hybridization of other materials into COFs has significantly enhanced their photocatalytic performance. This material effectively merges the strengths of two distinct components into an independent yet intricately designed structure, offering exceptional tunability that significantly boosts its photocatalytic performance. Zang et al. [81]. construct a novel hierarchical core-shell MOF@COF hybrid (Ti-MOF@TpTt) coated with ultra-thin COF nanobelt through a sequential growth strategy (Figure 6c). They reasonably controlled the ratio of Ti-MOF-CHO and TpTt-COF precursor, which realized the construction of ultra-thin nanobelt structure and afforded more accessible active sites. The as-obtained Pd decorated Pd@Ti-MOF@TpTt catalyst exhibited much higher photocatalytic performance (conversion of 99%, selectivity of 99%) than Ti-MOF, TpTt COF, and the hybrids with fibrillar-like COF-shell for the cascade reactions of ammonia borane hydrolysis and nitroarenes hydrogenation.

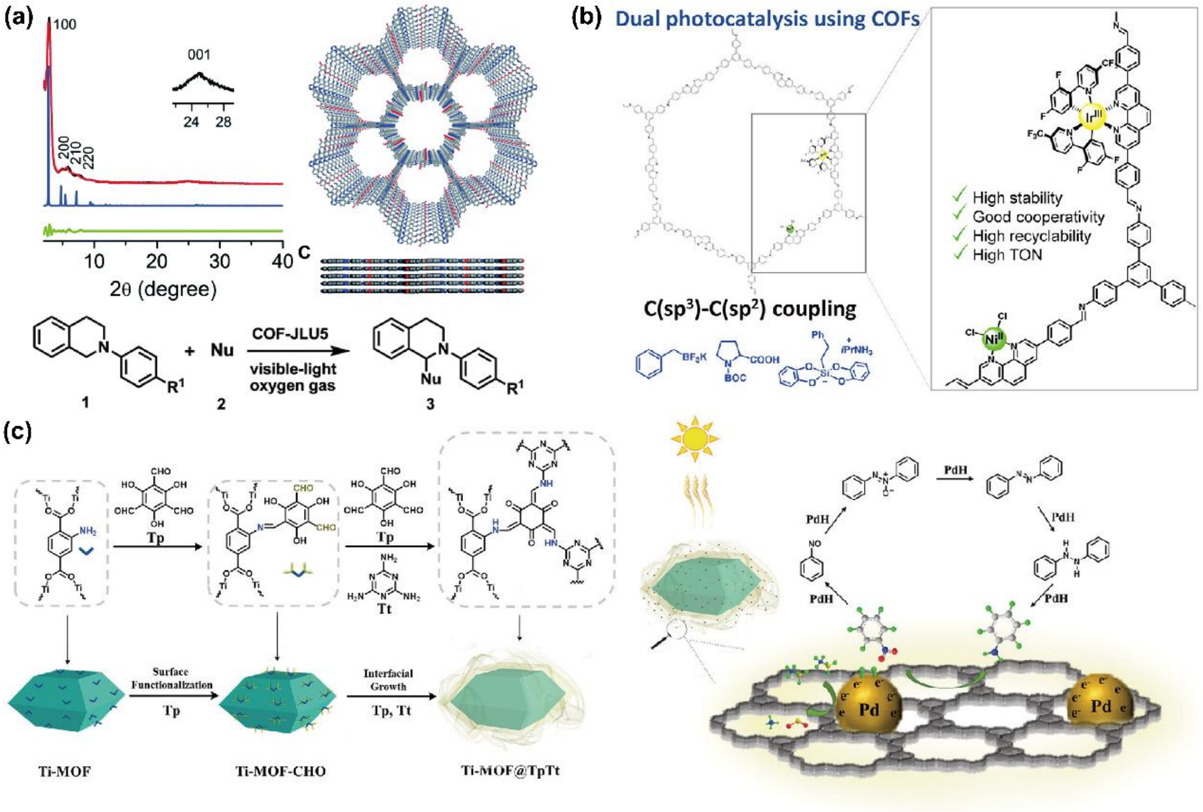

Figure 6. (**a**) Space filling models and photocatalytic C-C coupling reaction of COF-JLU5 [79]. Copyright © 2017 Royal Society of Chemistry. (**b**) Light-mediated cross-coupling of dual photocatalysis using COF [80]. Copyright © 2021 American Chemical Society. (**c**) The synthetic route of Ti-MOF@TpTt and the mechanism of nitrobenzene hydrogenation [81]. Copyright © 2021 Wiley-VCH GmbH.

5. Active Species

In recent years, photocatalytic organic transformation has shown great potential in photocatalytic synthesis, and semiconductor-based photocatalysts are the core of these catalytic systems. Understanding and mastering the active species of photocatalysts and photocatalytic systems that drive organic reactions under the action of light will help to build an efficient photocatalytic organic transformation system. According to the mechanism of the photocatalytic organic reaction process, we roughly divide the active species of these photocatalytic organic syntheses into electron, hole and free radical mechanisms [82,83]. When it comes to electrons and holes, as with other photocatalytic reactions, the photosensitizer absorbs photons with sufficient energy to generate excitons or carriers (electron-hole pairs). The photogenerated holes in the valence band and the photogenerated electrons in the conduction band directly interact with the matrix and additives in the system, leading to the occurrence of organic oxidation or reduction reactions.

Radicals are predominant reactive intermediates in photocatalytic organic reactions, including superoxide radicals, singlet oxygen, etc. [84]. In photocatalytic organic reactions involving oxygen, absorption of photons by photosensitizers generates excitons or electron-hole pairs, converting the photosensitizer to an excited state. The interaction between the excited-state photosensitizer and oxygen leads to the generation of reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$) and superoxide radicals ($O_2^{\bullet-}$) in Figure 7. These ROS are highly reactive and play a crucial role in driving the reaction. Compared with other photocatalytic reactions, photocatalytic organic synthesis produces a more important type of radicals, namely substrate radicals [85]. For example, halogen radicals and alkyl radicals in dehalogenation reactions are important reaction intermediates.

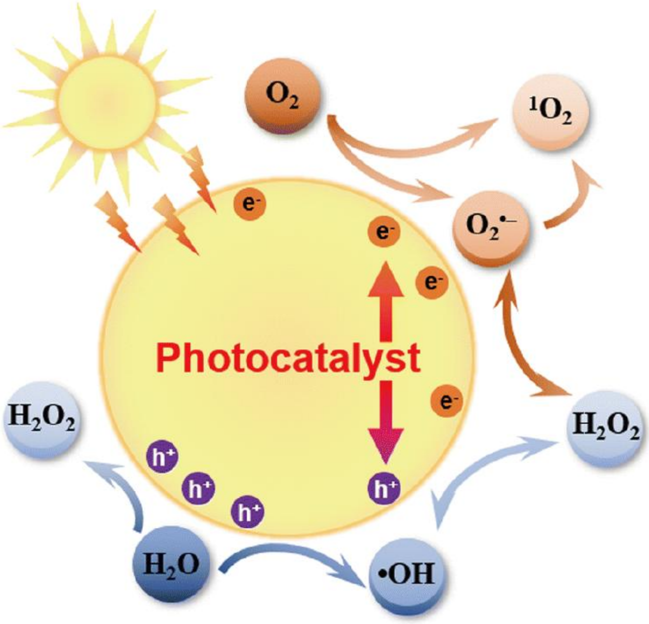

Figure 7. Schematic illustration of the generation of reactive oxygen species in photocatalysis [83]. Copyright © 2023 Royal Society of Chemistry.

5.1. Superoxide Radical ($O_2^{\bullet-}$)

The electrons in the conduction band of the semiconductor and the oxygen molecules adsorbed on the surface of the catalyst undergo a process of photogenerated electron transfer to the π* orbital of the oxygen molecules to generate superoxide radical ($O_2^{\bullet-}$). According to the energy band theory, molecular oxygen activation can only be realized when the conduction band potential of the semiconductor is lower than the standard redox potential of O_2/•O_2. As a moderate oxidant, $O_2^{\bullet-}$offers a controlled approach to oxidation reactions, with potential applications in selective organic transformations [86].

5.2. Singlet Oxygen ($^1O_2$)

Singlet oxygen ($^1O_2$) could be generated through the process of energy transfer and electron transfer [87]. The triplet excitons are generated in the semiconductor transfer energy to O_2 and make it spin flip to generate $^1O_2$. In another way, photoactivated holes can react with $O_2^{\bullet-}$to produce $^1O_2$ by electron transfer process. As a moderate oxidant compared with •OH and $O_2^{\bullet-}$, $^1O_2$ can effectively oxidize organic chemicals while avoiding the overoxidation.

5.3. Hydroxyl Radicals (•OH)

Hydroxyl radicals (•OH) could be generated through the molecular oxygen participation process and the hole oxidation process. In the molecular oxygen participation process, molecular oxygen first takes place to produce $O_2^{\bullet-}$ by the one-electron reduction reaction, and then $O_2^{\bullet-}$ can dissociate and hydrogenate to form •OH, but it requires so much energy barrier that it is usually difficult to occur. Generally, adsorbed water or surface-attached hydroxyls in photocatalyst could be oxidized by photogenerated holes to generate •OH [88]. Typically, •OH radical is widely considered to be the strongest oxide species in organic oxidation, which has a special effect on the oxidation of organic molecules with weak affinity to the catalyst surface.

6. Photocatalytic Organic Transformations

6.1. Reductive Dehalogenation

Halogenated hydrocarbons and halogenated aromatic compounds are a class of highly toxic pollutants that widely exist in the environment [89]. A viable approach to mitigating their environmental impact involves the conversion of carbon-halogen bonds into carbon-hydrogen bonds through hydrodehalogenation or reductive dehalogenation, accompanied by the release of halide ions. Photocatalytic dehalogenation has become the most promising method due to mild conditions, high selectivity and environmental consistent [90]. In recent, Kaskel et al. [91]. presented the photocatalytic performance of flexible MIL-53(Cr) in a dehalogenation reaction, The researcher discussed adaptive structural flexibility and dynamic pore structure of MIL-53(Cr) in the photocatalytic process, and the effects of solvents on substrate and product molecule (Figure 8a). Furthermore, the effects of dynamic structure, electronic configuration, solvent effect, substrate effect and host-guest interaction on the catalytic efficiency were elucidated, respectively. A model reaction in photocatalysis was proposed promising industrial applications for treating halogen-containing wastewater. Gao et al. [92]. reported two donor–acceptor COFs, TPE-BSD-COF and TPE-BD-COF that were constructed by a photoactive benzoselenadiazole and benzothiadiazole as a building block (Figure 8b). These traits indicate that the two COFs possess strong charge-transferring and separation abilities, leading to improved performance in photocatalytic debromination ability for α-bromoacetophenone. The novel TPE-BSD-COF and TPE-BD-COF with phenacyl bromide derivatives as substrates achieved 98% and 95% photocatalytic yields within 1 h, respectively.

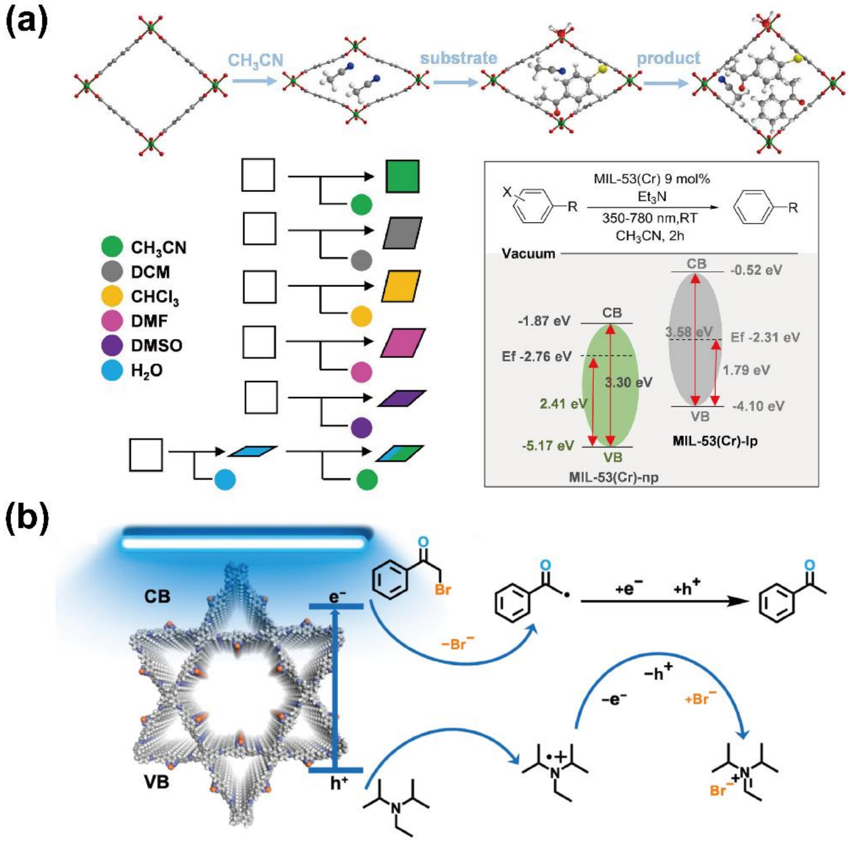

Figure 8. (**a**) The interaction between solvent and substrate drives the photocatalytic dehalogenation in flexible MIL-53 structure [91]. Copyright © 2025 Wiley-VCH GmbH. (**b**) Schematic diagram of TPE-BD-COF photocatalytic debromination reaction mechanism [92]. Copyright © 2024 MDPI.

6.2. Sulfide Oxidation

Sulfoxides play a significant role in organic synthesis and pharmaceutical development, as they are often synthesized via the oxidative conversion of thioethers under aerobic conditions [93]. In general, there are two reaction mechanisms for sulfoxides: electron transfer and energy transfer [94]. Shang et al. [95]. demonstrated electron transfer mechanism using the incorporation of a PDI unit into a COF, named PDI-PDA, by linking PDI with p-phenylenediamine (PDA) to achieve precise regulation of electron transfer kinetics (Figure 9a). PDI-PDA exhibits high catalytic efficiency for a variety of thioethers, including those with electron-donating and electron-withdrawing groups, which underscores its versatility as a catalyst. Compared to PDI-PH, PDI-PDA catalytic achieved a yield of 90.90% and 94.19% for methyl p-tolylthio-anisole and 4-methoxythioanisole photocatalytic oxidation. The researchers further demonstrated that the unique framework formed by PDI and PDA units has a high charge separation efficiency which promotes the generation of $O_2^{\bullet-}$ and thereby enhances photocatalytic efficiency. In terms of energy transfer, Dong et al. [96], reported that four COFs with adjustable photocatalytic properties were constructed at the atomic level using 2,4,6-triformyl-phloroglucinol (Tp) as a modular molecule, denoted as TpDz-COF, TpPa-COF, TpBpy-COF, TpBD-COF (Figure 9b). The introduction of N sites in the linkers improves the photocatalytic production capacity of the COFs to directly generate singlet oxygen from O_2. This effectively improves the photogenerated carrier transport efficiency of the COFs material, resulting in a significant increase in the activity and selectivity of photocatalytic sulfide oxidation, such as aromatic sulfides, aliphatic sulfides, and mustard gas sulfides. TpBpy-COF demonstrated superior photocatalytic activity investigated in the photocatalytic oxidation reaction, with a sulfoxide conversion and selectivity of up to 99.9%.

6.3. Oxidative Dehydrogenation

The selective oxidative dehydrogenation of alkanes to olefins is attracting increasing attention, and has been widely used in fine chemical industry, biomedicine and organic synthesis [97]. Typically, thermocatalysts operating at high temperatures are needed for C-H activation, which results in significant energy waste and side production. Thus, photocatalytic is a promising method for alkane-to-alkene conversions under mild conditions. Zhang et al. [98]. prepared a photocatalyst containing PdZn intermetallic nanoparticles supported on ZnO, which afforded the production rate from ethane dehydrogenation to ethylene was 46.4 mmol g^{-1} h^{-1}, and the ethylene selectivity was 92.6% under 365 nm irradiation. The strong electron transfer interaction is achieved at the PdZn-ZnO interface, and light radiation promotes the formation of $O_2^{\bullet-}$ active sites on the upper surface of ZnO. These sites activate the C-H bond in ethane and lead to the formation of ethylene and water (Figure 9c). Chen et al. [99]. reported a three-dimensional COF assembled based on N4, N4-bis(4′-amino-[1,1′-biphenyl]-4-yl)-[1,1′-biphenyl]-4,4′-diamine (TABPA) with high crystallinity and permanent pores, termed 3D-TABPA-COF (Figure 9d). The catalytically active center triphenylamine exposed in the pores is an effective photosensitizer, which can not only enhance the light absorption capacity, but also promote the rapid transfer of photogenerated electrons and ensure effective carrier separation. This unique structure and the active species produced $O_2^{\bullet-}$can effectively dehydrogenate 1,2,3,4-tetrahydroquinoline into quinoline with a conversion rate of more than 99.9%, when exposed to the visible light conditions of room temperature and pressure.

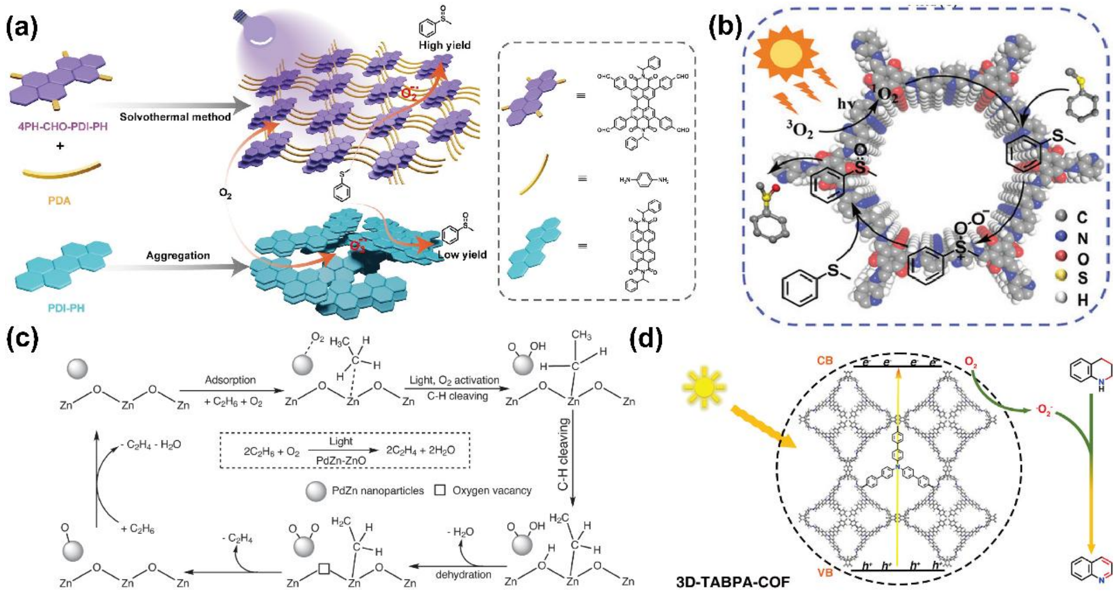

Figure 9. (**a**) Schematic diagram of PDI-PDA and PDI-PH in the photocatalytic oxidation of thioether [95]. Copyright © 2024 Wiley-VCH GmbH. (**b**) Schematic represented of the syntheses of Tp-based COFs and mechanism of photocatalytic thioanisole oxidation [96]. Copyright © 2024 Wiley-VCH GmbH. (**c**) Proposed reaction mechanism for photocatalytic ODHE over PdZn-ZnO [98]. Copyright © 2024 Springer Nature. (**d**) Photocatalytic oxidative dehydrogenation to quinoline over 3D-TABPA-COF [99]. Copyright © 2024 American Chemical Society.

6.4. C-C Couping

C-C coupling reactions play a crucial role in constructing complex molecular architectures, making them indispensable in the synthesis of pharmaceuticals, fine chemicals, and functional materials [100]. Conventional C-C cross-coupling reactions typically rely on high-temperature conditions and often depend on noble-metal-based catalysts. In contrast, photocatalytic C-C coupling reactions eliminate the need for extensive use of homogeneous catalysts, particularly noble-metal catalysts, aligning well with the principles of sustainable development. Zhang et al. [101]. obtained photoactive azulene-based conjugated microporous polymers P-Az-B by Suzuki cross-coupling reaction of 1,3-dibromoazulene with 1,3,5-phenyltriboronic acid tris(pinacol) ester with 1,3-dibromoazulene (Figure 10c). The researchers have demonstrated a novel photocatalytic Stille-type coupling reaction pathway using conjugated organic polymers P-Az-B to form aromatic C-C bonds. The aryl radicals generated by the oxidative destannylation of aryl stannanes are coupled with electron-activated aryl iodides, a maximum yield of 93%, and the driving force is the photogenerated electron / hole pair in the conjugated organic photocatalyst.

6.5. C-N Coupling

Imines play a significant role in the synthesis of dyes, pharmaceuticals, fine chemicals, and biologically active nitrogen-containing compounds [102]. The oxidative coupling of amines to imines using solar energy is an efficient route to solve above issues. Li et al. [103]. reported a robust covalently bonded direct Z-scheme heterostructure (PDI/mpg-CN) constructed by Perylenetetracarboxylic diimide (PDI) and graphitic carbon nitride (g-CN) for photocatalytic oxidative coupling of amines (Figure 10b). PDI molecules were covalently connected to the surface of mesoporous g-CN via an in-situ condensation strategy. The PDI/mpg-CN heterojunction is conducive to the spatial separation of photogenerated carriers through the Z-type transfer path, which has an excellent amine oxidation rate of 20.63 mmol g^{-1} h^{-1}, the significant oxidative coupling conversion efficiency and selectivity, and great cycle stability. Wang et al. [104]. designed and synthesized a fully conjugated donor-acceptor covalent organic framework Py-BSZ-COF, which is composed of an electron-donating pyrene unit and an electron-accepting benzothiadiazole unit. Py-BSZ-COF showed significant amine oxide coupling ability (Figure 10a). The formation of N-benzyl-1-phenylmethylaniline was observed in the benzylamine photocatalytic system, and the conversion rate was 99%.

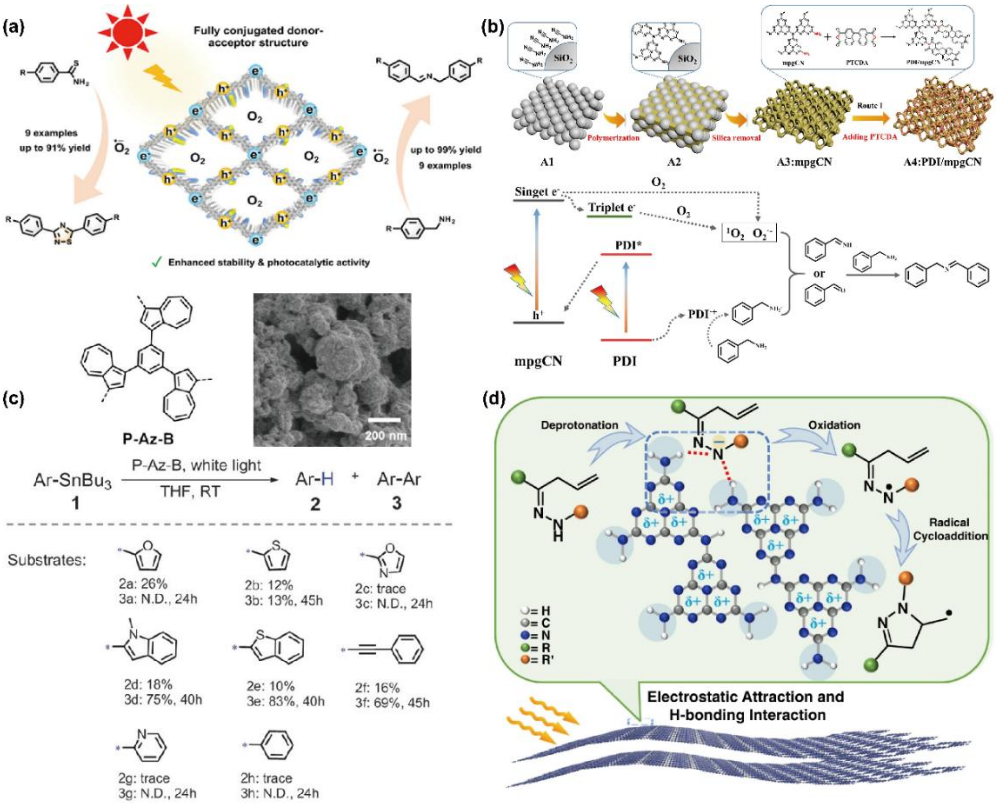

Figure 10. (**a**) Fully conjugated donor-acceptor Py-BSZ-COF for photocatalytic oxidative amine coupling [104]. Copyright © 2020 American Chemical Society. (**b**) Synthesis for PDI/mpg-CN heterostructure and photocatalytic oxidative coupling [103]. Copyright © 2021 Elsevier. (**c**) Photocatalytic C-C coupling reaction of various aryl using P-Az-B as photocatalyst [101]. Copyright © 2017 Wiley-VCH GmbH. (**d**) Interface assisted catalytic cyclization of nitrogen-centered radicals over carbon nitride [105]. Copyright © 2022 Springer Nature.

6.6. Cyclization Reactions

Intermolecular or intramolecular cyclization reactions are used to synthesize carbocyclic or heterocyclic rings. These reactions are widely employed in industrial processes and pharmaceutical development, enabling the production of high-performance polymer materials, highly potent therapeutic agents, and a diverse array of naturally occurring compounds. Wang et al. [105]. reported the synthesis of functionalized dihydropyrazoles from N-H hydrazones on CN (Figure 10d). Researchers have established that carbon nitride, which possesses rich in -NH_2 groups and relative positive surface charge, could effectively complex with deprotonated anionic intermediates and enhance the adsorption of organic reactants onto the catalyst surface. When using a series of β,γ-unsaturated hydrazones as the substrates, g-CN-U exhibits an efficient and stable catalytic performance for photocatalytic production of various pharmaceutically related heterocycles, including dihydropyrazoles, pyrazoles, with high yield and wide substrate range.

7. Conclusions and Outlooks

Photocatalytic organic reactions have rapidly become one of the most active fields in organic synthesis and pharmaceutical science, greatly contributing to energy conservation and utilization. In this review, we summarize the types of catalysts for photocatalytic organic reactions, including metal oxides, perovskites, small molecular organic semiconductors, carbon nitride, PDI, MOFs, COFs, etc. (Table 1). In the exploration of photocatalytic organic conversion, the reaction types have been extended to include various reactions, including oxidation, reduction, coupling, cyclization, polymerization and asymmetric reactions. With the in-depth study of photocatalytic organic reactions, researchers have also realized the importance of elucidating the reaction mechanism of photocatalytic organic conversion, and began to guide the design of photocatalysts or photocatalytic systems based on these mechanisms [106]. This will undoubtedly guide researchers to synthesize value-added organic chemicals in a more scientific, reasonable and functional way in the future. However, despite significant progress has been made in photocatalytic organic reactions recently, the following may be areas of high opportunity and significance that require further research and solutions:

(1) The rational design of catalysts is crucial for photocatalysis. Although a variety of photocatalyst materials have been developed, it is crucial to precisely control the photocatalytic efficiency and selectivity at the atomic level and in heterostructures, because slight adjustment in the band structure could have a significant effect on the catalytic behavior. In this case, by adjusting the microenvironment, energy band, and heterostructure of the photocatalytic material, it is beneficial for the charge separation and the synergistic effect between multiple active sites. Furthermore, the morphology, defects, and other factors of the photocatalyst need to be further explored to determine its photocatalytic behavior.

(2) Crystallinity, stability and recyclability have always been the necessary conditions for the industrial application of heterogeneous photocatalysts. Although some metal oxides have good stability and recyclability, there is still a long way to go to realize industrial application. Since the continuous exploration of some new materials, such as MOFs, COFs, stability and cyclicity are an unavoidable problem. Recently, some methods have been reported to improve the crystallinity and stability, including exploring some new building blocks, new connection methods, adding additional regulators, selecting better catalysts, new synthesis strategies, and constructing single crystals. The improvement of stability and recyclability for the catalyst is still an urgent problem to be solved in the industrialization process.

(3) Compared with other photochemical reactions, photocatalytic organic conversion has a complex substrate reaction pathway, resulting in a variety of products and reduced selectivity. However, in order to meet the needs of practical applications, it is necessary to ensure the selectivity of the product through appropriate catalyst design or adjustment of reaction conditions for further use.

(4) Despite the photocatalyst has achieved the conversion of a series of organic reactions, most of the reactions are relatively simple and lack practical applications. Therefore, exploring more novel and high value-added organic reactions is an important research direction in the development of photocatalysts, such as aromatization reaction, cyclization reaction, inert C-H activation, asymmetric synthesis and biomimetic synthesis. Using modern physical and chemical characterization methods, machine learning and theoretical simulation methods to achieve chiral photocatalytic simulation, and assist in guiding the realization of asymmetric photochemical organic synthesis. Therefore, it is of great significance to construct photofunctionalized chiral photocatalysts and develop asymmetric photocatalytic organic reactions.

(5) The in-depth study of the photocatalytic mechanism can further guide the design of efficient catalyst systems. It is worth noting that the current understanding of the photocatalytic mechanism is poor due to the lack of experimental evidence and advanced characterization techniques. In recent years, the development of

characterization techniques and theoretical calculations also provides a means for in-depth study of the reaction mechanism. With the support of a series of in situ characterization techniques such as in situ X-ray absorption spectroscopy, the in situ work of the catalyst also provides the possibility to verify the actual reaction intermediates and obtain unprecedented catalytic mechanisms. More directly, *in-situ* electron microscopy could visualize materials and provide an opportunity to directly observe the conversion of active sites or the generation of reaction intermediates during the reaction.

Table 1. Summary of photocatalysts for organic transformations performance.

	Catalyst	Conditions	Reaction Types	Performance	Ref.
Inorganic semiconductors	TiO_2	365 nm LED	Aerobic oxidation of benzene to phenol	Yield: 8% Selectivity: 93%	[63]
	TiO_2 heterogeneous	11 W 400−800 nm CFL lamp	C−H arylation	Yield:96%	[64]
	WO_3 nanosheets	λ > 400 nm	Benzylamine coupling	Conversion: 80% Selectivity: >99%	[66]
	Porous 2D-CdSe	150 W λ > 420 nm Xenon lamp	C-X (X is a halogen) to C-D	Yield: 93%	[67]
	$CsPbBr_3$	12 W 455 nm Blue LED	C-C Bond formation N-Heterocyclization C-O Cross-Coupling	Yield: 84% Yield: 90% Yield: 85%	[68]
	PdZn-ZnO	100 W 365 nm LED	Ethane dehydrogenation	46.4 mmol g^{-1} h^{-1} Selectivity: 92.6%	[98]
Organic semiconductors	mpg-CN	455 nm LED	C-H Bifunctionalization of arenes	Yield: 67%	[71]
	Th-BT-Th	460 nm LED	C-H functionalization	Conversion: >99% Yield: 90%	[72]
	PDIs	420 nm LED	N-heterocycles oxidation	Yield: 84%	[73]
	P-Az-B	white LED	Stille-Type Coupling	Yield: 80%	[101]
	PDI/mpg-CN	λ > 420 nm Xenon lamp	Benzylamine coupling	Conversion: 99% Selectivity: 97%	[103]
	g-CN-U	420 nm LED	Nitrogen-centered radical cyclization	Yield: 80%	[105]
MOFs	Pt/PCN-224(M)	λ > 400 nm, 100 mW/cm^2	Benzyl alcohol oxidation	Yield: >99%	[75]
	ZJU-56	660 nm LED	Benzylamine coupling	Conversion: 62%	[76]
	MIL-53	350–780 nm	Dehalogenation	Yield: 86%	[91]
COFs	COF-JLU5	30 W 460 nm LED	C-N Coupling	Yield: 92%	[79]
	Ir,Ni@Phen COF	23 W 450 nm LED	C-C Cross-Coupling	Yield: 90%	[80]
	Pd@Ti-MOF@TpTt	300 W Xe lamp	Nitrobenzene hydrogenation	Conversion: >99% Selectivity: >99%	[81]
	TPE-BD-COF	18 W blue LED	Dehalogenation	95%	[92]
	PDI-PDA	410–420 nm LED	Thioether oxidation	Yield: 90.4%	[95]
	TpBpy-COF	24 W 460 nm LED	Thioether oxidation	Conversion: 99% Selectivity: 95%	[96]
	3D-TABPA-COF	6 W 405 nm LED	Dehydrogenation	Conversion: 99.9%	[99]
	Py-BSZ-COF	15 W 520 nm LED	Benzylamine coupling	Conversion: 99% Selectivity: 99%	[104]

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