



Control of selectivity in organic synthesis via heterogeneous photocatalysis under visible light

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ABSTRACT

Organic synthesis driven by heterogeneous catalysis is a central research theme to both fundamental research and industrial production of fine chemicals. However, the employment of stoichiometric strong oxidizing or reducing reagents (e.g., $K_2Cr_2O_7$ and $LiAlH_4$) and harsh reaction conditions (e.g., high temperature and pressure) always leads to the products of overreaction and other by-product residues (e.g., salt and acid waste). Thus the poor control of product selectivity and tremendous energy consumption result in the urgent demand to develop novel technologies for heterogeneous catalysis. Given the current global theme of development in CO_2 reduction and sustainable energy utilization, one promising protocol is heterogeneous photocatalysis. It enables sustainable solar-to-chemical energy conversion under mild conditions (e.g., room temperature, ambient pressure, and air as the oxidant) and offers unique reaction pathways for improved selectivity control. To accurately tailor the selectivity of desired products, the electronic structure (e.g., positions of valence-band maximum and conduction-band minimum), geometric structure (e.g., nanorod, nanosheet, and porous morphology), and surface chemical micro-environment (e.g., vacancy sites and co-catalysts) of heterogeneous photocatalysts require rational design and construction. In this review, we will briefly analyze some effective photocatalytic systems with the excellent regulation ability of product selectivity in organic transformations (mainly oxidation and reduction types) under visible light irradiation, and put forward opinions on the optimal fabrication of nanostructured photocatalysts to realize selective organic synthesis.

KEYWORDS

organic synthesis, selectivity control, heterogeneous photocatalysis, photocatalyst design, visible light irradiation

1 Introduction

Oxidation and reduction reactions are of vital importance in organic chemistry [1]. Taking the carbon center as an example, the oxidative transformation of concerned organic compounds can be regarded as a process where a carbon atom bonds to more electronegative elements such as oxygen [2]. Instead, reduction corresponds to the bonding between the carbon atom and less electronegative elements such as hydrogen [3]. The roughly simplified definition aims to help distinguish oxidation and reduction cases in many organic transformations. These redox organic reactions afford effective protocols to synthesize valuable bulky and fine chemicals, involving the precursors or intermediates of dyes, drugs and polymers. To speed up the reactions, usually the presence of a catalyst is essential. Among various catalytic modes (e.g., heterogeneous, homogeneous and biological catalysis), heterogeneous catalysis prevails in industrial organic chemistry due to several remarkable advantages, including facile separation between organic products and catalysts, continuous-mode operation, and scalable production [4, 5]. Notably, no matter what kinds

of catalytic systems are employed, one key evaluation indicator always dominates especially in the field of fine chemicals, that is the selectivity of desired products [6]. High selectivity not only provides the high purity of final products, but also reduces the cost of removing byproducts. In contrast, the undesired overoxidation or overreduction leads to low-value products, coke deposition, or even mineralization with the emission of useless CO_2 [7, 8]. Therefore, it is one main scientific subject in organic chemistry how to precisely control selectivity.

For instance, 5-hydroxymethyl furfural (HMF) oxidation to furan-2,5-dicarboxylic acid (FDCA) has attracted much attention in oxidative organic transformations [9]. It is well known that HMF can serve as a platform chemical produced from renewable biomass [10], while its oxidation product FDCA shows prospective applications as a green alternative to terephthalic acid for the synthesis of biopolymers [11]. Actually, 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HFCA) and 5-formyl-2-furancarboxylic acid (FFCA) as expensive intermediates (Fig. 1(a)) during the oxidation process also play vital roles in the synthesis of pharmaceuticals, pesticides, polymers and functional materials [12–15]. However,

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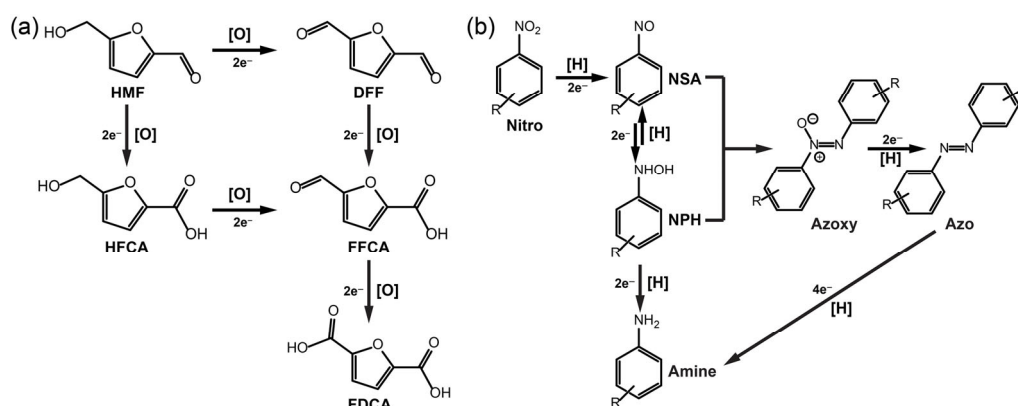


Figure 1 (a) Reaction paths for the oxidation of HMF to FDCA with DFF, HFCA and FFCA as intermediates. (b) Reaction paths for the reduction of nitro compounds to amines, azoxy and azo products (NSA = nitrosoarene, NPH = N-phenylhydroxylamine).

the preparation of each product requires the utilization of quite different catalytic systems. For example, vanadium, ruthenium and manganese-based catalysts (e.g., V_2O_5/C , Ru/C and $Mn_{0.7}Cu_{0.05}Al_{0.25}O_x$) can drive the oxidation of HMF to DFF in the neutral solvents [16–18], while noble metal systems (e.g., Pd/TiO_2 , Pt/Al_2O_3 and Au/TiO_2) with a basic environment (adding NaOH) are usually demanded for the production of FDCA [19–21]. In addition, the HMF molecule has a non-negligible problem of instability in solution. It can facilitate dehydrate to levulinic acid and formic acid at lower pH, while the polymerization takes place easily to form undesired humins at higher pH possibly due to the acetal reaction between the hydroxymethyl and aldehyde group of HMF [22]. As such, it remains challenging to manipulate the selective production of these valuable intermediates in a single catalytic system via the simple adjustment of external reaction conditions (e.g., reaction atmosphere, temperature or oxidative species).

On the other hand, in reductive organic transformations, nitroaromatics have been investigated widely due to their valuable reduction products such as amines and azo/azoxy compounds, which can serve as precursors for the preparation of nitrogen-containing polymers, pharmaceuticals, dyes and liquid crystal materials [23, 24]. As shown in Fig. 1(b), the deep reduction product is an amine, while the nitroso arene, hydroxylamine and azo/azoxy compounds act as intermediates. It is a challenge to tailor the reduction degree of nitroaromatics with the active intermediates as final products. The use of strong reducing reagents such as hydrazine, $NaBH_4$ and H_2 always results in the overreduction with amines formed, even though versatile heterogeneous catalysts varying from metals [25, 26], metal oxides [27, 28] and sulfides [29] to metal-free nanocarbons [30] have been explored. Therefore, novel milder catalytic systems should be developed to control the selectivity for the production of desired intermediates such as highly expensive azo/azoxy compounds.

At present, heterogeneous photocatalysis has emerged as one promising synthetic tool for selective organic reactions, which can be performed under visible light irradiation with mild conditions such as room temperature and ambient pressure [31–39]. Thus far, various effective heterogeneous photocatalytic systems have been established for selective organic transformations, such as the tunable oxidation of inert C–H bonds and reductive coupling of nitro groups in organic compounds [40–43]. Huge efforts have been invested into accurately regulating the electronic structures, geometric structures and surface chemical micro-environment of

heterogeneous photocatalysts. These properties of photocatalysts serve as key factors for influencing the selectivity of desired organic products, as they directly involve the important steps, including light absorption, charge separation, reactant diffusion/activation, product desorption and surface reaction paths [44].

2 Fundamental principles of heterogeneous photocatalysis

Commonly, the semiconductor-based photocatalysts demonstrate two categories: (1) photocatalyst materials with a wide bandgap ($E_g > 3$ eV), including TiO_2 [45], ZnO [46] and Ta_2O_5 [47], which can only absorb ultraviolet (UV) light; (2) narrow-bandgap photocatalysts ($E_g \leq 3$ eV) that can make use of visible light (e.g., $BiVO_4$ [48], CdS [49], C_3N_4 [50] and $TaON$ [51]). More cases are presented in Fig. 2(a), illustrating their bandgaps and band positions. In addition, the solar radiation spectrum in Fig. 2(b) shows visible and infrared light account for more than 90% of the whole solar energy. For this reason, the development

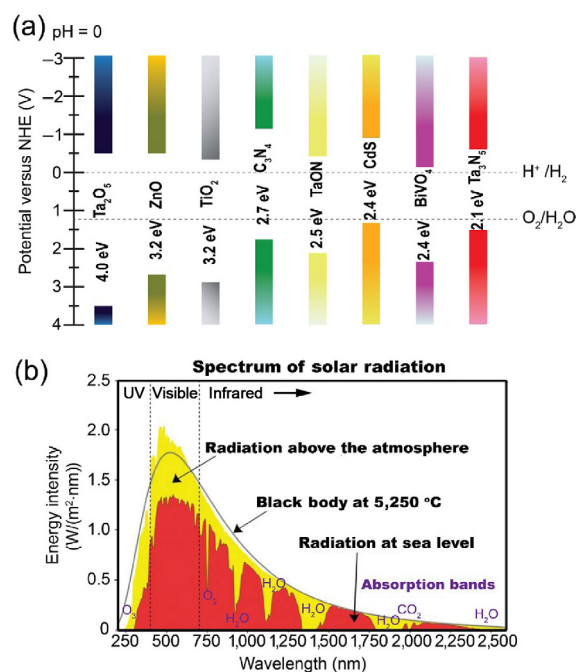


Figure 2 (a) The bandgaps and band positions of several common semiconductors. (b) The solar radiation spectrum. Image obtained from <https://www.e-education.psu.edu>.

of photocatalysts with narrow bandgaps should be vigorously promoted for more efficient utilization of solar energy. It is noteworthy that a narrow-band photocatalyst is actually not always favorable in photocatalytic applications even though it can represent better light absorption, given that the photo-generated holes and electrons are demanded to have proper oxidation and reduction power, respectively. In detail, the valence-band maximum (VBM) position should be more positive than the potential of the oxidative half reaction, while the conduction-band minimum (CBM) position should be more negative than the potential of the reductive half reaction. To this end, the bandgaps and band positions of photocatalysts require fine tuning to match desired organic reactions.

In photocatalytic reactions, the used photocatalyst serves as a dual role during the whole catalytic process: (1) charge source from light absorption and (2) reactive sites for adsorbed reactants on the surface. The fundamental principle of semiconductor-based photocatalysis is depicted in Fig. 3(a). Initially, the semiconductor is excited by light, possessing the photon energy equal to or larger than the bandgap (E_g). Electrons in the filled valence band (VB) thus jump to the empty conduction band (CB) with holes left in the VB (step (1) in Fig. 3(a)). Subsequently, the photo-generated electrons and holes are separated and transported from bulk to the surface of the semiconductor (steps (2) and (3)). On the surface, electrons and holes will reduce electron acceptors and oxidize electron donors for desired reactions, respectively (steps (4) and (5)). In the meantime, electrons and holes have the possibility to recombine with each other with the energy released as luminescence or heat (step (6)). From the view of a time scale, the initial light absorption occurs within femtoseconds ($\sim 10^{-15}$ s), while the other steps proceed much more slowly. Ideally, in the absence of electron acceptors and donors, the recombination of electron-hole pairs can take place within 10–100 ns ($\sim 10^{-9}$ s). Obviously, the slowest step involves the surface catalytic reactions, requiring microseconds to

milliseconds (10^{-6} to 10^{-3} s) [52]. Therefore, photocatalysis basically runs via two processes: (1) the photon–electron conversion process within a nanosecond time scale, including the above-mentioned steps (1–3) and (6); (2) the surface catalytic reactions with a microsecond time scale or even longer (steps (4) and (5)).

In addition to the above traditional semiconductor-based photocatalysts, another class of fascinating nanomaterials called plasmonic photocatalysts has also attracted much attention recently [53, 54]. These plasmonic cases make use of the localized surface plasmon resonance (LSPR) effect from Ag, Au or Cu nanospheres, presenting visible absorption bands at ~ 400 , ~ 530 or ~ 600 nm, respectively [55]. The LSPR phenomenon can be regarded as a collective photon-induced resonant oscillation of the free electrons in metals. It takes place when the frequency of incident photons matches the oscillation frequency of surface electrons, which resonates against the restoring force from the positive nuclei [55]. Since the successful cases for photocatalysis in 2008 via Au/ZrO₂ [56] and Ag@AgCl [57], plasmonic nanomaterials have received increasing interest. Figure 3(b) shows one typical working mechanism of a metal/semiconductor photocatalyst with the plasmonic nanostructure for redox reactions. Briefly, the electrons below the Fermi level (E_f) of the metal are excited to the surface plasmon (SP) states (step 1) with hot holes left after light absorption, which then can transfer to the CB of the semiconductor (step 2). Later, the plasmon-generated hot electrons and holes can respectively drive the reduction (step 3) and oxidation (step 4) [58]. The termed hot electrons (holes) refer to the charges out of thermal equilibrium with the atoms in a nanomaterial. In parallel, the hot charges can transfer energy to the phonon modes of nanoparticles, which induces the photothermal process with the local temperature of metal surface increasing dozens of degrees Celsius [59].

Generally, by virtue of photo-generated charges, O₂ and H₂O molecules can involve the generation of reactive oxygen species (ROS) such as hydroxyl radical ($\cdot\text{OH}$), superoxide anion ($\text{O}_2^{\cdot-}$), hydrogen peroxide (H₂O₂) and singlet oxygen $^1\text{O}_2$ (shown in Fig. 4) [60]. The ROS and oxidative holes can drive the selective oxidation of diverse functional groups in organic compounds (e.g., hydroxyl and aldehyde groups). Because of the different oxidation powers from these oxidative species, the controlled oxidation of organic compounds can be realized via the facile change of external reaction environment (e.g., aerobic/anaerobic and hydrous conditions). Meanwhile, the addition of alcohols (e.g., isopropanol), amines or even H₂O can serve as hydrogen donors for the selective reduction

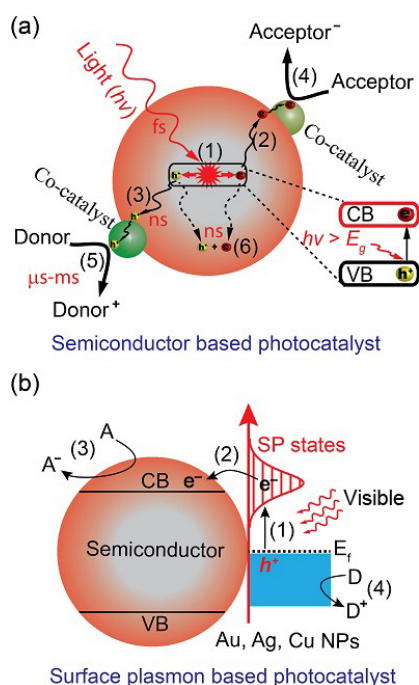


Figure 3 Fundamental working principles of (a) semiconductor-based photocatalysts and (b) surface plasmon-based photocatalysts. (Reproduced with permission from Ref. [31], © Royal Society of Chemistry 2014).

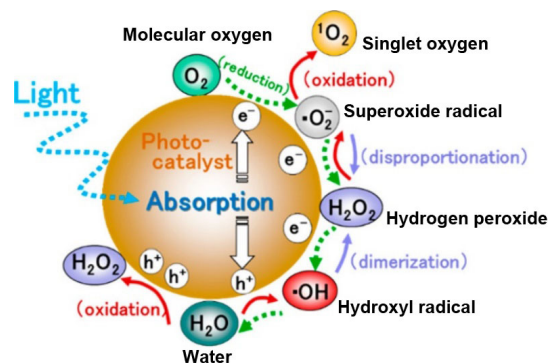


Figure 4 Reactive oxygen species from the photocatalytic reduction and oxidation of O₂ and H₂O. (Reproduced with permission from Ref. [63], © American Chemical Society 2017).

with the assistance of holes and electrons from photocatalysts [61, 62]. Due to a much weaker reductive ability than the strong reducing reagents like NaBH_4 , the electrons located at CBM level can precisely tailor the gradual hydrogenation of organic compounds (e.g., nitro, alkyne or aldehyde/ketone groups) instead of the undesired overreduction. In the following sections, we will analyze the established heterogeneous photocatalytic systems for selective redox organic transformations under visible light illumination, and focus on the electronic/geometric structures and surface chemical micro-environment of nanostructured photocatalysts.

3 Tuning selectivity in redox organic reactions via heterogeneous photocatalysis

Impressively, a variety of organic reactions have been successfully driven by diverse heterogeneous photocatalysts, such as the Suzuki coupling [64], Heck reaction [65], α -alkylation of aldehydes [66], epoxide alcoholysis [67, 68], Diels-Alder cycloaddition [69], fatty acid decarboxylation [70] and Aldol condensation [71]. In comparison with the above-mentioned reactions, we will focus on the typical redox types in this review, which involve a few intermediates during the oxidation and reduction processes. Furthermore, the control of selectivity in organic synthesis via heterogeneous photocatalysis can be comprehensively analyzed. For example, in oxidation cases, inert C–H bonds can be gradually oxidized to hydroxyl, aldehyde/ketone or carboxylic acid groups via bismuth oxyhalide [40], CdS [72] or halide perovskite-based photocatalysts [41, 73]. Similarly, nitroarenes can be selectively reduced to azoxy, azo and amine compounds by use of polymeric C_3N_4 [42] or plasmonic Cu nanoparticles [74].

3.1 Oxidation

3.1.1 C–H bond activation

The selective oxidation of $\text{C}(\text{sp}^3)\text{--H}$ bonds by use of O_2 to value-added oxygenated products (e.g., aldehydes/ketones and carboxylic acids) is one of the most important reactions in industrial organic chemistry. Taking toluene oxidation as an example, the employment of harsh reaction conditions such as high reaction temperature (160 °C) and O_2 pressure (up to 1.7 MPa) leads to poor selectivity control with 55% of

benzaldehyde, 30% benzyl alcohol, and 13% benzoic acid [75]. Moreover, similar results are obtained when the strong oxidizing reagent *tert*-butyl hydroperoxide (TBHP) is used at a lower reaction temperature (80 °C) [76]. Instead, heterogeneous photocatalysis can realize the oxidation of toluene to benzaldehyde or benzoic acid with high selectivity under mild conditions (air, room temperature and visible light irradiation).

Li research group has successfully prepared the photochromic $\text{Bi}_2\text{WO}_{6-x}$ /amorphous BiOCl nanosheets (*p*-BWO) [40], presenting a remarkably promoted photocatalytic performance in toluene oxidation. The *p*-BWO nanosheets were synthesized via a hydrothermal method with $\text{Bi}(\text{NO}_3)_3$ and Na_2WO_4 as precursors and octadecyltrimethylammonium chloride (OTAC) as a surfactant. The addition of OTAC surfactant allows controlling the thickness of *p*-BWO nanosheets and offers photochromic properties by introducing the Cl element. By controlling the irradiation time (Fig. 5(a)), different main oxygenated products can be produced with high selectivity. For example, selectivity of 91% for benzaldehyde can be achieved with a yield of 25% at the reaction time of 3 h. The increase of reaction time up to 6 h leads to the production of some benzoic acid (accounting for ~ 10%) with benzaldehyde still dominating (selectivity 81%). After 48 h irradiation, the benzoic acid presents as the main product (selectivity of 70%) with benzaldehyde as the rest product. The proposed photocatalytic mechanism is shown in Fig. 5(b). The holes at the VBM position of 2.33 V (vs. normal hydrogen electrode (NHE) at pH = 7) can oxidize the toluene molecules to produce benzyl radicals, which quickly combine with O_2 to form peroxy species (ROOH). Meanwhile, the electrons at CBM of -0.45 V can reduce O_2 to superoxide anion, which promotes mild oxidation. The formed ROOH compound is unstable and easily dehydrated into benzaldehyde and H_2O . The excellent stability of *p*-BWO photocatalyst renders the continuous oxidation of benzaldehyde to benzoic acid with the help of holes/electrons and O_2 . Thus the presence of charges with suitable oxidation/reduction powder and O_2 play vital roles in the selective oxidation of C–H bonds. The reversible transformation between $\text{W}(\text{v})$ and $\text{W}(\text{vi})$ offers the efficient trapping of electrons to enhance the carrier separation and catalyst stability, displaying the photochromic effect. Moreover, plenty of $[\text{W}(\text{vi})\text{O}_{6-x}]$ units due to abundant crystalline-amorphous boundaries can promote the adsorption of toluene reactant via the coordination between

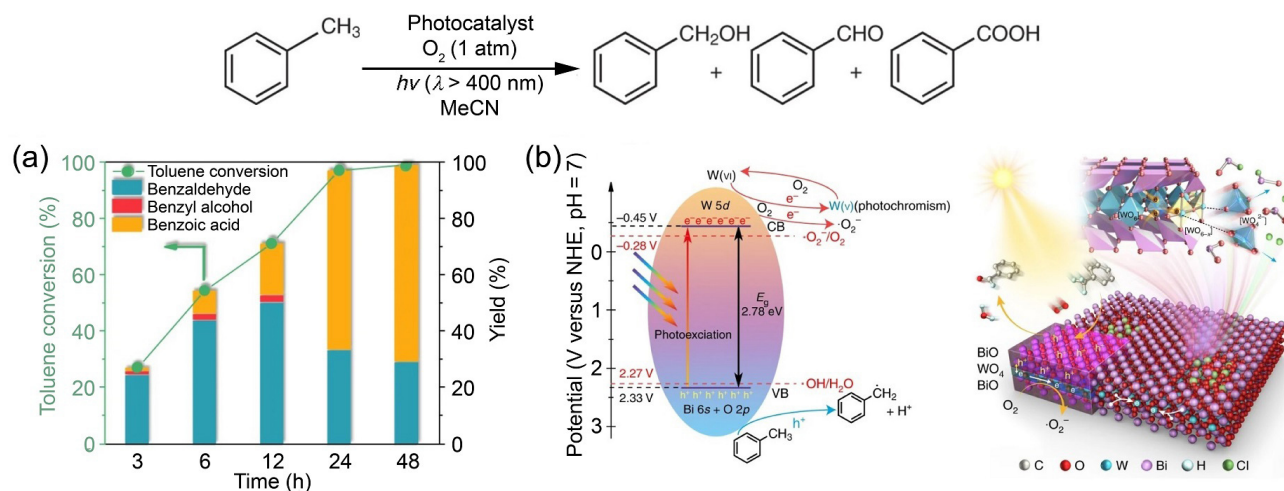


Figure 5 (a) The typical reaction performance in toluene oxidation via *p*-BWO photocatalyst. (b) The band structure of *p*-BWO with the plausible photocatalytic mechanism. (Adapted with permission from Ref. [40], © Cao, X. et al. 2018).

the benzene ring and tungsten metal sites. However, it remains unclear whether this efficient photocatalytic system can drive the selective oxidation of more inert aliphatic alkanes (e.g., *n*-hexane). The large bandgap of *p*-BWO photocatalyst (~ 2.8 eV) also means moderate light absorption with an absorption edge located at 440 nm, which can be further optimized for better utilization of solar energy.

In addition, Yuan et al. have used a sol-gel method to prepare a BiOBr/TiO₂ composite for activating C–H bonds under visible light irradiation [77]. Notably, the surface chlorination can boost the photocatalytic activity to yield oxygenated products (aldehydes or ketones) in comparison with the bare BiOBr/TiO₂ composite. For example, the estimated apparent quantum efficiency (AQE) for the photocatalytic oxidation of toluene into oxygenated products was reported to reach 15.3% (at $\lambda = 430 \pm 25$ nm) over the surface-chlorinated BiOBr/TiO₂. The chlorination was facily realized by impregnating the BiOBr/TiO₂ composite in HCl solutions with different concentrations (from 0.12 to 1.2 mol/L), which can tune the chlorine content on the surface of BiOBr/TiO₂. Based on the mechanism study, the superior photocatalytic activity can be ascribed to the combined contributions from both chlorine radicals and holes to form more alkyl radicals. Subsequently, the alkyl radicals can react with O₂ to form ROOH intermediates, which undergo fast dehydration to produce aldehydes or ketones. This photocatalytic system implies that the surface chemical environment of photocatalysts is crucial to mediating the catalytic activity and selectivity in organic transformations.

Other photocatalyst materials including CdS and halide perovskites have been developed as well to drive the selective oxidation of C(sp³)–H bonds to aldehydes/ketones [41, 72, 73, 78–83]. For example, as early as 2012, the Xu research group utilized the spheric CdS semiconductor (prepared via a simple precipitation method using Cs(AC)₂·2H₂O and Na₂S·9H₂O as precursors) for toluene oxidation with 100% selectivity towards benzaldehyde [72]. Later, CdS flowers with ultrathin nanosheets (~ 0.8 nm) demonstrated a similar photocatalytic performance (Fig. 6(a)), which was synthesized under hydrothermal conditions with decanoic acid as a ligand and potassium orthoethyl xanthate as a sulfur source [84]. The addition of hole and superoxide anion scavengers suppresses the activity significantly, suggesting the useful oxidative species mainly as photogenerated holes and O₂. The absence of benzoic acid is probably ascribed to the weaker oxidation ability of holes at VBM of ~ 1.7 V in the case of CdS [80]. For halide perovskite nanomaterials, both lead-based (e.g., NiO_x/FAPbBr₃/TiO₂ [79]) and lead-free (e.g., Cs₃Bi₂Br₉ [41, 83] and Cs_xMA_{3-x}Sb₂Br₉ [73]) photocatalysts can oxidize toluene to benzaldehyde and benzyl alcohol at room temperature in air under visible light irradiation. For instance, the photocatalyst cell NiO_x/FAPbBr₃/TiO₂, was prepared through an antisolvent precipitation approach by adding the *N,N*-dimethylformamide solution with FAPbBr₃ precursors into the toluene suspension containing TiO₂ and NiO_x sheets. This photocatalyst cell employs holes to trigger the C–H activation with the selectivity of 83% to benzaldehyde and 17% to benzyl alcohol. The non-negligible amount of benzyl alcohol may result from the lifted VBM level up to ~ 1.0 V (Fig. 6(b)) [79].

In comparison, Dai et al. have reported that the stronger oxidative power from all-inorganic bismuth based halide perovskite Cs₃Bi₂Br₉ photocatalyst affords a higher selectivity to benzaldehyde (90%), whose VBM level locates at ~ 2.2 V (Fig. 7(a)) [41]. This efficient supported photocatalyst Cs₃Bi₂Br₉/

SBA-15 was easily prepared via an impregnation method, involving the mild drying of a mesoporous silica SBA-15 support well wetted with the dimethylsulfoxide (DMSO) solution containing CsBr and BiBr₃ precursors. Moreover, a series of control experiments were conducted to reveal the roles of photoinduced charges and possible intermediates, whose results are shown in Fig. 7(b). The *tert*-butanol (TBA) as a hydroxyl radical scavenger demonstrates no influence on the photocatalytic activity. This suggests the absence of $\cdot\text{OH}$, which always causes the non-selective oxidation of organic compounds to CO₂/CO and water instead of valuable organic products [60]. Furthermore, the ultra-small Cs₃Bi₂Br₉ nanoparticles (2–5 nm) confined in the pore channel of mesoporous silica support (SBA-15) show a substantially lower photoluminescent intensity in contrast to the bulk material (Figs. 7(c) and 7(d)), indicating the suppressed radiative recombination of electron–hole pairs. The shorter diffusion path of excited charge carriers on small nanoparticles may lead to this enhanced charge separation. The nanostructure of Cs₃Bi₂Br₉ phase also introduces rich bismuth sites with under-coordinated states, presenting a strong electronic interaction with the benzene ring of toluene. This unique adsorption behavior has been supported by the emerging visible light absorption bands (500–750 nm) when various arenes (e.g., benzene, toluene and aniline) attach Cs₃Bi₂Br₉ nanoparticles (Fig. 7(e)). The theoretical calculations reveal the close distance (around 2.9 Å) between hydrogen atoms from the –CH₃ group and Br atoms on the surface of Cs₃Bi₂Br₉ nanoparticles (Fig. 7(f)), which facilitates the holes from Br sites to activate C–H bonds. Based on the thorough investigation of reaction mechanisms as shown in Fig. 7(g), the photogenerated holes from Br atoms can cleave C–H bonds to form alkyl radicals, which quickly react with O₂ to produce the peroxy species (ROO $\cdot$). In this perovskite system, ROO $\cdot$ may subsequently combine with reducing species (H⁺/e[−]) on perovskite surface to generate the ROOH intermediate, which

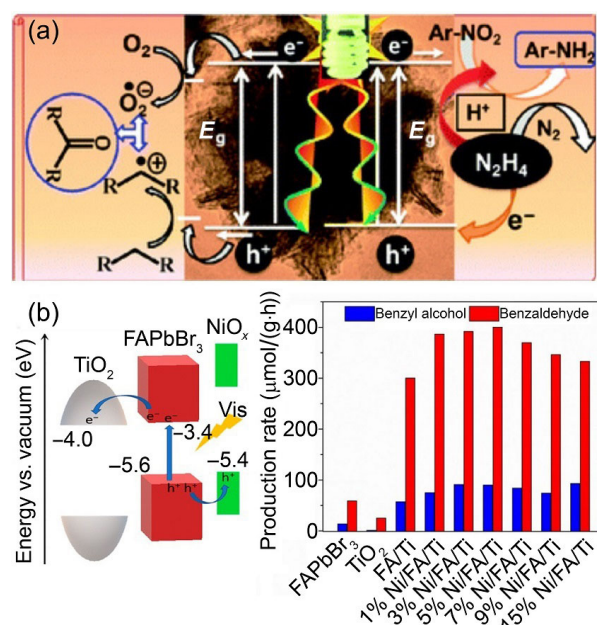


Figure 6 (a) CdS photocatalyst for toluene oxidation. (Reproduced with permission from Ref. [84], © Royal Society of Chemistry 2015). (b) NiO_x/FAPbBr₃/TiO₂ photocatalyst cell with the production rates of oxygenates. (Reproduced with permission from Ref. [79], © American Chemical Society 2019).

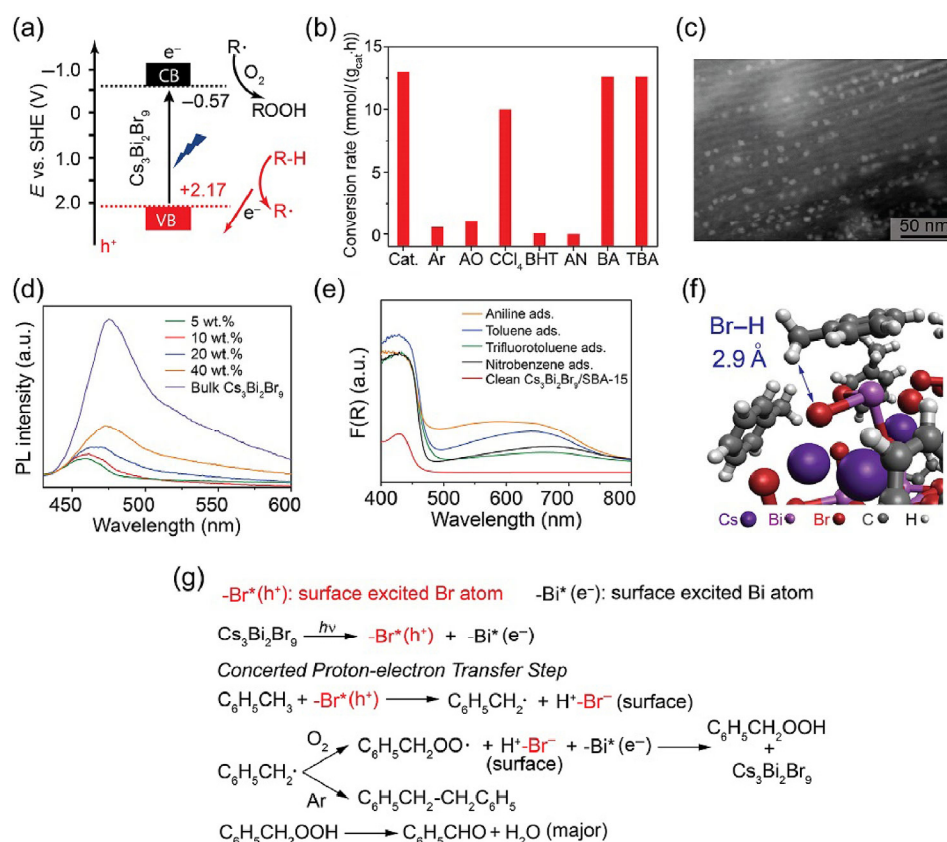


Figure 7 (a) The band structure of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ halide perovskite-based photocatalyst. (b) The influence of various scavengers (e.g., ammonium oxalate (AO), CCl_4 , butylated hydroxytoluene (BHT), aniline (AN), benzoic acid (BA) and *tert*-butanol (TBA)). (c) The transmission electron microscopy image of ultra-small $\text{Cs}_3\text{Bi}_2\text{Br}_9$ nanoparticles in the pore channels of SBA-15. (d) Photoluminescence data of supported and bulk $\text{Cs}_3\text{Bi}_2\text{Br}_9$ materials. (e) UV-vis absorption profiles for $\text{Cs}_3\text{Bi}_2\text{Br}_9$ nanoparticles with different arenes adsorbed. (f) The calculated model focused on Br-H geometry. (g) The plausible photocatalytic mechanism for C-H bond activation via the $\text{Cs}_3\text{Bi}_2\text{Br}_9$ photocatalyst. (Adapted with permission from Ref. [41], © Dai, Y. T. et al. 2020).

can be further dehydrated to carbonyl products according to the *in-situ* diffuse reflectance infrared Fourier transform spectroscopy experiments. Additionally, the energy barrier of C-H bond activation step on $\text{Cs}_3\text{Bi}_2\text{Br}_9$ nanoparticle equals the energy difference between reactants (toluene on excited surface $-\text{Br}^*(h^+)$) and intermediates ($\text{PhCH}_2^{\cdot}$ on $-\text{Br}^-\text{H}^+$ surface). Based on theoretical calculations, this C-H bond activation initiated by holes (on Br atoms) as a concerted proton-electron transfer process is thermodynamically feasible.

Even though this bismuth-based halide perovskite can drive the oxidation of linear aliphatic alkanes to oxygenated products with high selectivity ($\geq 99\%$ for total products), the regioselectivity is still quite poor with a mixture of different aldehydes/ketones and alcohols. Thus, when the reactant molecule has more than one similar reactive site, it is challenging to attack the designated one with high regioselectivity in heterogeneous photocatalysis. Another common problem in the photo-oxidation of C-H bonds is that alcohol is unable to be generated as a dominant product since alcohol is more active than inert alkane reactants. It is a challenging task for heterogeneous photocatalysis how to convert alkanes into alcohols without further oxidation, which may require the fine adjustment of oxidative species and desorption behavior of alcohol intermediates via tuning the surface chemical micro-environment of photocatalysts.

3.1.2 Alcohol/aldehyde oxidation

As illustrated in the Introduction part, HMF with the coexistence

of one hydroxyl and one aldehyde group, as a versatile platform chemical, can be oxidized to diverse products such as DFF, HFCA, FFCA and FDCA. These valuable products can be applied in several fields such as polymers, pharmaceuticals and other functional materials (Fig. 8) [85].

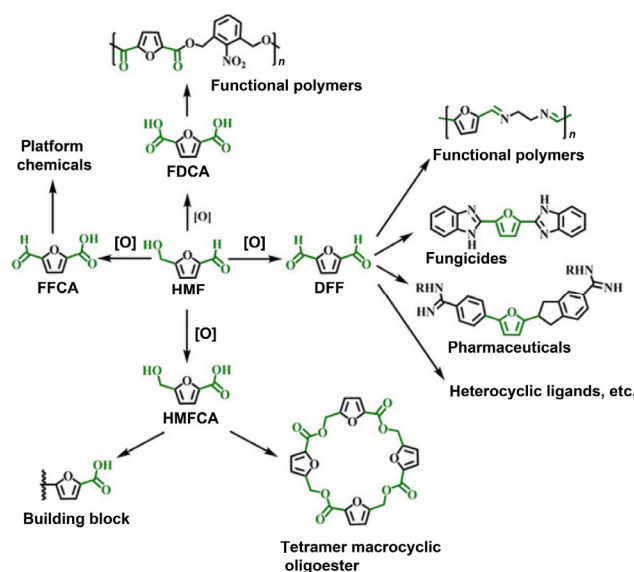


Figure 8 Applications of various products from the oxidation of HMF. (Reproduced with permission from Ref. [85], © Wiley-VCH GmbH 2020).

In heterogeneous photocatalysis, different ROSs have been well utilized to control selectivity during the photo-oxidation of HMF [86]. One typical example is the photocatalyst of cobalt thiorphyrzine (CoPz) on polymeric $g\text{-C}_3\text{N}_4$ (CoPz/ $g\text{-C}_3\text{N}_4$), which has been established by Zhang and Deng research groups in 2017 [87]. Due to the strong electronic interaction between CoPz and $g\text{-C}_3\text{N}_4$, the robust CoPz/ $g\text{-C}_3\text{N}_4$ photocatalysts were prepared via a simple mixing-adsorption method with certain amounts of CoPz and $g\text{-C}_3\text{N}_4$ dispersed in CH_2Cl_2 solvent, which underwent evaporation to obtain the desired CoPz/ $g\text{-C}_3\text{N}_4$ powders. It has been found that the selectivity towards DFF and FDCA can be controlled by the system pH as shown in Figs. 9(a) and 9(b). In the alkaline environment (pH = 9.18), the FDCA can be produced with a high selectivity up to 97% after 14 h light irradiation. In contrast, a slightly acidic solution (pH = 4.01) renders DFF as the main product (yield above 80%). The time-dependent reaction performance also indicates that DFF is the possible intermediate when HMF is oxidized to FDCA. The high pH can speed up the cleavage of C–H bonds in hydroxyl or aldehyde groups, thus providing the possibility to dwell on DFF intermediate in acidic conditions. On the other hand, without deposition of CoPz co-catalyst, bare $g\text{-C}_3\text{N}_4$ only presents the mineralization of HMF to CO_2 and H_2O . To investigate the reaction mechanism behind this satisfactory selectivity control, electron paramagnetic resonance (EPR)

experiments have been conducted (Fig. 9(c)). $^1\text{O}_2$ has been directly detected in the case of CoPz/ $g\text{-C}_3\text{N}_4$ while $\cdot\text{OH}$ is observed in bare $g\text{-C}_3\text{N}_4$. $^1\text{O}_2$ as the main oxidative species can realize the quantitative oxidation of aldehydes to carboxylic acids or selective conversion of alcohols to carbonyl products [88, 89]. On the contrary, $\cdot\text{OH}$ as the strongest ROS can completely destroy the furan structure of HMF. Therefore, the perfect combination of $^1\text{O}_2$ ROS species and environmental pH adjustment leads to the selective oxidation of HMF to DFF and FDCA with high yields in air under ultraviolet–visible (UV–vis) light irradiation. Based on the mechanistic study, a tentative photocatalytic mechanism for the HMF oxidation has been addressed as shown in Fig. 9(d). After the strong absorption of visible light from the photocatalyst CoPz/ $g\text{-C}_3\text{N}_4$, the CoPz units bonded on $g\text{-C}_3\text{N}_4$ transfer energy to triplet O_2 ($^3\text{O}_2$), which is converted into the active $^1\text{O}_2$. As such, $^1\text{O}_2$ with suitable oxidation capability can selectively oxidize HMF to FDCA. However, the more precise regulation with HFCA or FFCA as the main product has not been realized in CoPz/ $g\text{-C}_3\text{N}_4$ photocatalytic system.

As shown in Table 1, the use of holes or superoxide anions ($\text{O}_2^{\cdot-}$) can drive the selective oxidation of HMF to DFF, HFCA or FFCA (selectivity over 85%) via different photocatalytic systems under visible light irradiation [90–99]. Several photocatalysts such as $\text{Fe(III)/Bi}_2\text{MoO}_6$, plasmonic Au/TiO_2 and $g\text{-C}_3\text{N}_4/\text{NaNbO}_3$ composite have been developed to

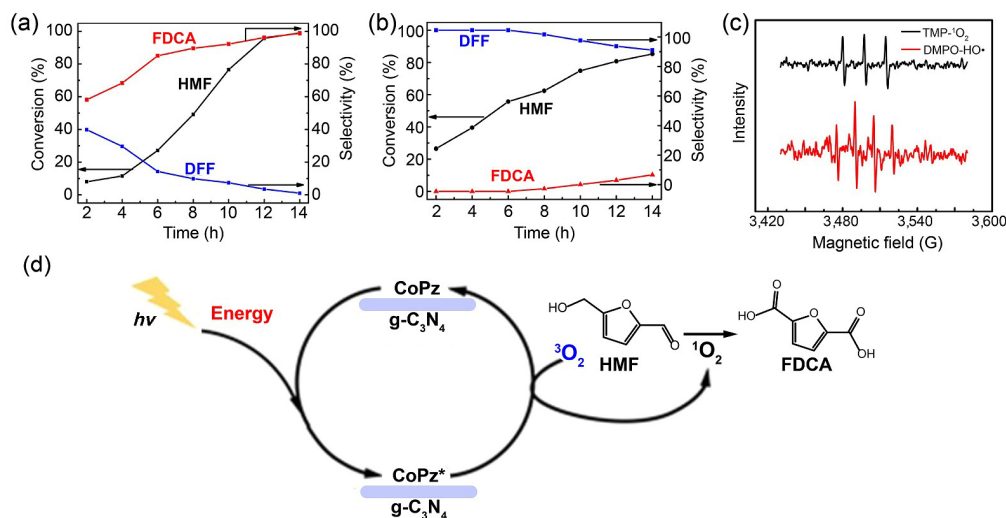


Figure 9 The time-dependent reaction performance from CoPz/ $g\text{-C}_3\text{N}_4$ photocatalyst with the pH at (a) 9.18 and (b) 4.01. (c) The EPR signals with 2,2,6,6-tetramethylpiperidine (TMP)- $^1\text{O}_2$ and dimethyl pyridine N-oxide (DMPO)-OH $\cdot$ adducts detected. (d) A plausible photocatalytic mechanism for the photo-oxidation of HMF to FDCA. (Adapted with permission from Ref. [87], © American Chemical Society 2017).

Table 1 Photocatalysts for the selective oxidation of HMF to DFF, HFCA or FFCA

Photocat.	Light	Oxidative species	Product	Con. (%)	Sel. (%)	Ref.
TiO_2	515 nm	$\text{O}_2^{\cdot-}$	DFF	59	87	[90]
$\text{Fe(III)/Bi}_2\text{MoO}_6$	> 400 nm	$\text{h}^+/\text{O}_2^{\cdot-}$	DFF	32.6	95.3	[91]
CdS	448 nm	$\text{NO}_3^{\cdot-}$	DFF	—	99	[92]
Au/TiO_2	420–780 nm	$\text{O}_2^{\cdot-}$	HFCA	99	96	[93]
Ag/TiO_2	> 420 nm	$\text{h}^+/\text{O}_2^{\cdot-}$	HFCA	40	96.7	[94]
$\text{Au}_{0.5}\text{Ru}_{2.5}/\text{RGO}$	Xe lamp (full spectrum)	$\text{O}_2^{\cdot-}$	DFF	95.7	95	[95]
$g\text{-C}_3\text{N}_4\text{-H}_2\text{O}_2$	Sunlight	$\text{O}_2^{\cdot-}$	DFF	20	88	[96]
$g\text{-C}_3\text{N}_4\text{-NaNbO}_3$	> 400 nm	$\text{O}_2^{\cdot-}$	FFCA	35.8	87.4	[97]
CTF-Th@SBA-15	460 nm	$\text{h}^+/\text{O}_2^{\cdot-}/^1\text{O}_2$	DFF	57	99	[98]
MAPbBr_3	450 nm	$\text{h}^+/\text{O}_2^{\cdot-}/^1\text{O}_2$	DFF	100	90	[99]

generate the mild oxidative species. The presence of plasmonic metals like Au and Ag can lead to the production of HFCA while the modification of Au nanoparticles with Ru metal species tunes the selectivity towards DFF. As such, the mass ratio of Au and Ru in alloy significantly influences the product selectivity. More DFF is formed by increasing Ru content. The fast occurrence of HMF to HFCA on supported Au monometallic nanoparticles may be ascribed to preferable adsorption of the aldehyde group in HMF. Similar regulation of selectivity has been observed in the Au-Pd/CNT catalyst for the thermal oxidation of HMF [100]. This clearly demonstrates the importance of surface chemical micro-environment (e.g., exposed metal species) of photocatalysts to selectivity control. Interestingly, the incorporation of NaNbO_3 into C_3N_4 phase can dramatically enhance the selectivity of FFCA product. The highest selectivity (87.4%) of FFCA can be obtained after 8 h irradiation when the molar ratio between C_3N_4 and NaNbO_3 reaches 59.6%. However, prolonging reaction time up to 10 h leads to the decrease of selectivity for FFCA (~56%) with the generation of FDCA compounds (selectivity of ~25%), which indicates the presence of oligomer byproducts as well. Overall, it still lacks a photocatalytic system which can facily switch the production of DFF, HFCA, FFCA or FDCA. More efforts should be devoted to optimizing the electronic/geometric structures and surface catalytic sites of heterogeneous photocatalysts, which can afford the generation of effective oxidative species and proper adsorption sites.

3.1.3 Alkene epoxidation

Epoxides (e.g., propylene oxide) are widely used as important intermediates for the production of many bulky and fine chemicals, including polymers, perfumes and pharmaceuticals [101]. For instance, the annual production of propylene oxide (PO) reaches 10 million tons with a high market value (\$10.5 billion in 2017) [102], which is mainly used to manufacture polyurethane and propylene glycols [103]. Usually, epoxides are produced via the alkene epoxidation process, involving the employment of various oxidants such as *tert*-butyl hydroperoxide, H_2O_2 [104] and O_2 [105]. As shown in Fig. 10 (taking propylene as an example), alkene can be oxidized into

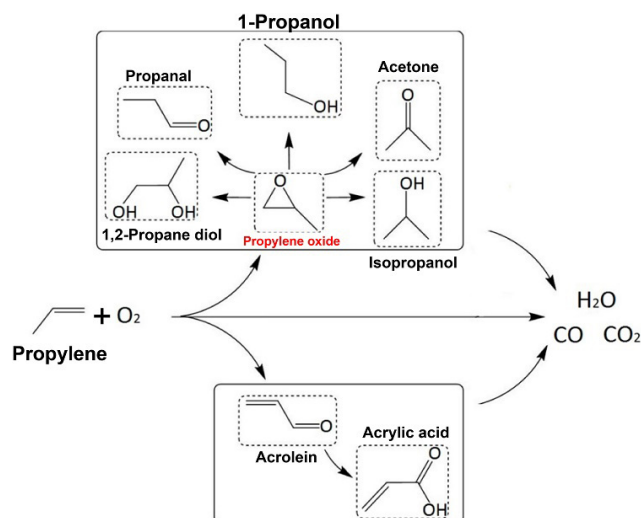


Figure 10 Possible products from the total and partial oxidation of propylene. (Reprinted with permission from Ref. [106], © American Chemical Society 2020).

diverse oxygenates including epoxides, aldehydes/ketones, alcohols and even undesired CO_2/CO . Over the past decades, heterogeneous metal catalysts (Cu, Ag, Cu, etc.) have been thoroughly explored for epoxidation with the assistance of active oxygen species [106]. However, selectivity is always the major problem, which decreases remarkably when the conversion increases especially in the cases with O_2 as the oxidant.

One promising solution appears when a visible light-mediated photocatalytic system is introduced. As early as 2001, rutile TiO_2 was tested for the epoxidation of 1-decene by use of H_2O_2 [107], which presents higher selectivity towards 1,2-epoxydecane under visible light irradiation ($\lambda > 440 \text{ nm}$) than UV light. The active sites may originate from the generation of a $\text{Ti}-\eta^2$ -peroxide on the surface after H_2O_2 treatment. Another successful case was reported in 2017 by the Zhu research group [108], who have developed a photocatalyst with Cu nanoparticles supported on titanium nitride (Cu@TiN , Fig. 11(a)). The Cu@TiN photocatalyst was prepared via an impregnation–reduction method, which loads CuO/Cu on TiN powders with the assistance of a fresh NaBH_4 solution in the first step. After the subsequent reduction at 300°C in a H_2 flow, the CuO/Cu@TiN powder was converted to the desired Cu@TiN photocatalyst. Importantly, the metallic Cu nanoparticles (with a mean size of 4 nm) well dispersed on TiN can be stable in air, which may be contributed to the charge exchange between Cu nanoparticles and the TiN support based on density functional theory calculations. The mechanism studies reveal that ethereal solvents (e.g., 1,4-dioxane)

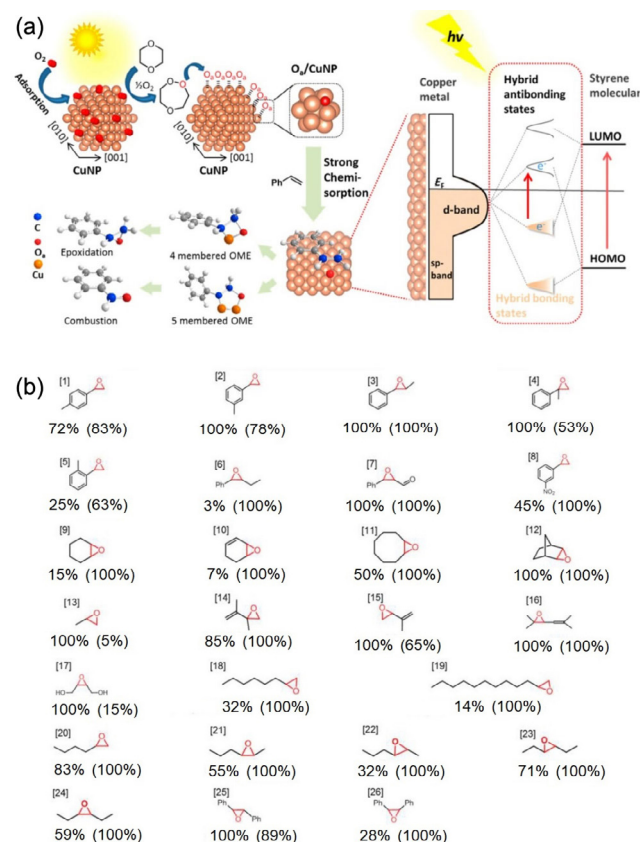


Figure 11 (a) The overall reaction paths of styrene epoxidation on Cu@TiN . (b) The epoxidation scope of various alkenes over Cu@TiN with selectivity values in bracket. (Adapted with permission from Ref. [108], © American Chemical Society 2017).

react with O_2 on the surface of Cu nanoparticles to yield the active oxygen adatoms (O_a), which can further oxidize activated alkenes to epoxides (Fig. 11(a)). Meanwhile, styrene strongly chemisorbs on the Cu surface to generate a Cu-styrene surface complex. This chemisorption can lead to the hybridization of Cu and styrene orbitals with the formation of bonding and antibonding states. Correspondingly, the light irradiation could initiate the direct resonant photoexcitation of electrons from the hybrid bonding state to the antibonding state, which triggers the interaction between styrene and O_a adatoms. The selective oxidation of styrene taking place on the Cu surface experiences a four-membered oxametallacycle (OME-4) intermediate, offering the desired epoxidation product. In contrast, another competing reaction path involving a five-membered OME (OME-5) can lead to undesired combustion products. Moreover, as shown in Fig. 11(b), various alkenes have been selectively oxidized to the corresponding epoxides by O_2 under visible light irradiation at low temperatures (40–60 °C).

Notably, the selectivity is significantly influenced by the chemical oxidation state of Cu. The active Cu@TiN photocatalyst shows a dropping epoxidation selectivity (from 85% to 65%) after a few cycling runs, which is attributed to the appearance of CuO. Another drawback of this Cu@TiN photocatalytic system can be observed in the case of propylene epoxidation, which demonstrates 5% selectivity with a full conversion of propylene and ketone as the main product. Thus it is a key research direction for the design of novel photocatalytic systems how to maintain the chemical properties of active sites and efficiently promote the epoxidation of short-chain alkenes (e.g., ethylene and propylene). The Linic research group has already elaborately combined the plasmonic properties of Cu nanoparticles with *in-situ* reduction of surface CuO_x shell back to metallic Cu [109]. It can sharply increase the steady-state selectivity of PO after visible light illumination during the thermal process (Figs. 12(a) and 12(b)). This study provides a useful protocol to maintain the reductive state of surface atoms during the oxidation reaction

(Figs. 12(c) and 12(d)), which is critical for selectivity control. Specifically, the core-shell nanoparticles with a plasmonic core (e.g., Cu, Ag or Au) can tune the chemical states of metal shell atoms through the LSPR-mediated photoreduction. However, the requirement of a high-level light intensity threshold (550 mW/cm²) may bring problems in the design of a scalable setup with more expenditure and technical challenges.

In addition, some other photocatalysts, including Pd/ZnO [110], AuCu/ZnO [111], cyano-group modified C_3N_4 [112], and Mo [113] or SnO_2 [114] decorated C_3N_4 , have been established for the selective epoxidation of styrene. The selectivity can be well manipulated via controlling the composition of co-catalysts or surface functional groups. For instance, using Au/ZnO leads to the 100% selectivity of benzaldehyde in the oxidation of styrene with O_2 . The introduction of Cu atoms to form AuCu alloy can boost the selectivity of styrene oxide up to 53% [111]. This promotion in the epoxidation of styrene can be ascribed to the presence of metallic Cu species, which are stabilized by the Au element. Unfortunately, the stability is still limited by the oxidation of metallic Cu after photocatalytic epoxidation. Another interesting case is the photocatalyst of C_3N_4 with cyano groups incorporated [112]. The cyano-group modified C_3N_4 was prepared by pyrolysis of the mixed precursors containing thiourea and trithiocyanuric acid at 550 °C in a muffle furnace. In comparison with bare C_3N_4 , the cyano-group modified C_3N_4 presents a higher selectivity toward styrene oxide (65% vs. 40%). The cyano group can regulate the formation of ROS, where O_2^- is converted to the active peroxy or 1O_2 species selectively adsorbed on the cyano group. Then the activated styrene can react with these ROSs to form a four-membered ring intermediate, leading to enhanced photocatalytic epoxidation. The experimental data in this study indicate that the selectivity mainly depends on the local structure of active sites (cyano group) rather than photoelectric properties (minor contribution). Moreover, the C_3N_4 -based photocatalyst exhibits excellent stability without yield decrease after 5 recycling tests. Even an up-scaled reaction (100 g styrene in 2.7 L solution) can be successfully performed under sunlight. After bubbling 1.5 L O_2 per day for half a month, the conversion of styrene reaches 99% with high selectivity (> 82%) of styrene oxide.

3.2 Reduction

3.2.1 Nitroarene hydrogenation

The deep reduction of nitro compounds to amines has been well accomplished by many photocatalytic systems, such as TiO_2 [115–118], CdS [119–121], metal-organic framework [122] and Bi_2MoO_6 [123]. In contrast, the more expensive products such as azo- and azoxy-compounds via mild reduction are difficult to be generated with high selectivity. According to the reaction paths shown in Fig. 1(b), the condensation between two active intermediates (nitroso-arenes and hydroxylamines) is essential for the production of azo-/azoxy-arenes. Therefore, the careful adjustments on the combination of nitroso-intermediate adsorption and reductive power from photocatalysts can be promising research directions.

A few studies focused on plasmonic Au nanoparticles have successfully realized the reductive coupling of nitrobenzene to azoxy- or azo-benzene under visible light irradiation [124–128]. For example, in the presence of a strong base (e.g., KOH), Au/ZrO₂ can produce azo-products from nitro compounds

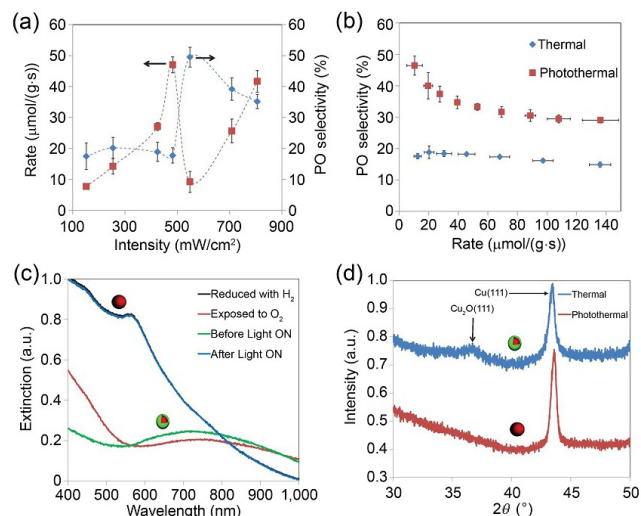


Figure 12 (a) Rate of propylene conversion and selectivity of PO related to the light intensity. (b) PO selectivity for thermal (no light) and photothermal (light on) processes at different reaction rates. (c) *In-situ* UV-vis absorption profiles for the catalyst 2%Cu/SiO₂ with different treatments. (d) X-ray diffraction patterns of the catalyst used in thermal and photothermal cases. (Reproduced with permission from Ref. [109], © American Association for the Advancement of Science 2013).

with high selectivity up to 99% via the hydrogen transfer from isopropanol [124]. The photocatalyst was prepared with the help of NaBH_4 reducing reagent to load Au nanoparticles with a mean size of 6 nm on ZrO_2 support. The oscillating electrons due to LSPR from Au nanoparticles can interact strongly with the electrophilic nitro or nitroso groups, which facilitates the following reductive coupling to form azo compounds (Fig. 13(a)). This strong adsorption of N–O bonds guarantees

high selectivity towards azo compounds. Moreover, the further reduction of azo products to amines is totally prohibited due to the insufficient reduction power from plasmonic Au. To better regulate the selectivity between azoxy- and azo-products, the supports of Au nanoparticles have been tuned via a doping strategy. With $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot n\text{H}_2\text{O}$ layered double hydroxide (HT) as the support prepared from a sol-gel process, phosphate anions (PO_4^{3-}) and different metal cations (e.g., Ga^{3+} , Fe^{3+} , and Zn^{2+}) have been introduced to tailor the interaction between HT and supported Au nanoparticles (Fig. 13(b)) [128]. Among the photocatalyst screening, $\text{Au}/\text{PO}_4^{3-}\text{-Ga}^{3+}\text{-HT}$ presents the best performance with excellent selectivity of azoxy-product ($> 99\%$). This effective prevention of azoxy to azo may relate to the presence of positive surface charges on Au, which can appear when hot electrons are transferred to HT support in the presence of PO_4^{3-} species as indicated in Fig. 13(c). The Au surface with positive charges weakens the affinity of electrophilic N–O bonds, thereby promoting the desorption of azoxy-products to avoid further reduction. Another feasible protocol for the selectivity control is to vary the reductive power of supported plasmonic metals. For instance, the Cu nanoparticle-based photocatalyst presents a high yield of azobenzene (96%) [74], while the modification of Cu with Ag renders azoxybenzene as the main product (selectivity of 86%) due to the limited reductive capability [129].

On the other hand, the “conventional” semiconductor-type photocatalysts such as C_3N_4 and BiOX also demonstrate the high selective reduction of nitro compounds to the corresponding azo- or azoxy-products. By using different light wavelengths, Dai et al. have developed a metal-free C_3N_4 based photocatalytic system to switch the reduction products between azoxy- and azo-compounds with isopropanol as the hydrogen donor [42]. The C_3N_4 was facilely obtained via a pyrolysis process of urea at 550°C in a Muffle oven, which can be scaled up to synthesize hundred grams of C_3N_4 photocatalysts. As shown in Fig. 14(a), the blue light irradiation ($\lambda = 450\text{ nm}$) leads to the production of azoxybenzene with an excellent yield (92%), while high selectivity of azobenzene (94%) can be achieved when purple light-emitting diode (LED) light ($\lambda = 410\text{ nm}$) is used. More impressively, the up-scaled photocatalytic system (up to 80 L volume) can maintain high selectivity towards azoxybenzene ($\sim 90\%$) under sunlight illumination (Fig. 14(b)). Importantly, the selective production of azoxy- or azo-compounds can be ascribed to the enhanced affinity of aromatic molecules via the π - π coupling effect from the tri-s-triazine unit in C_3N_4 . This unique adsorption can promote the N–N coupling reaction between nitroso- and hydroxylamine intermediates. Furthermore, the effective regulation of selective switch between azoxy- and azo-products mainly originates from the kinetic control of reduction processes via the accumulated amount of photoinduced charges. More charges on C_3N_4 under purple light irradiation can quickly reduce azoxybenzene to azobenzene prior to the desorption of azoxy-compound. In contrast, the slower reaction rate under blue light renders azoxybenzene as the main product at a certain reaction time point. The less steric hindrance from a nitro compound with one benzene ring also ensures its full conversion in both cases. Regarding the photocatalytic reaction mechanism, the C_3N_4 photocatalyst firstly generates charges after visible light excitation with the holes oxidizing the alcohol solvent (e.g., isopropanol) to carbonyl products in the presence of KOH . Subsequently, the abstracted hydrogen atoms from alcohols in combination with photogenerated

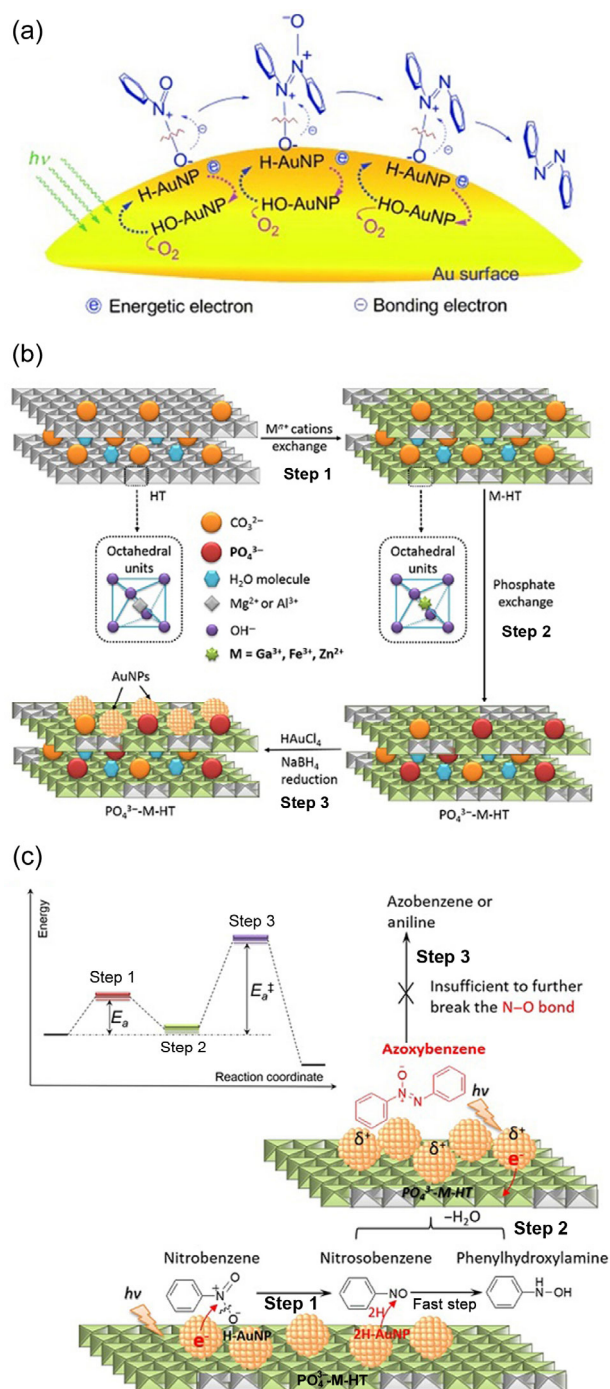


Figure 13 (a) Plausible mechanism for the photocatalytic reduction of nitroaromatic compounds over Au/ZrO_2 . (Reprinted with permission from Ref. [124], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2010). (b) Preparation of $\text{Au}/\text{PO}_4^{3-}\text{-M-HT}$ photocatalyst. (c) Proposed mechanism for the photocatalytic reductive coupling of nitrobenzene on $\text{Au}/\text{PO}_4^{3-}\text{-M-HT}$ under light irradiation. (Reproduced with permission from Ref. [128], © Elsevier B. V. 2017).

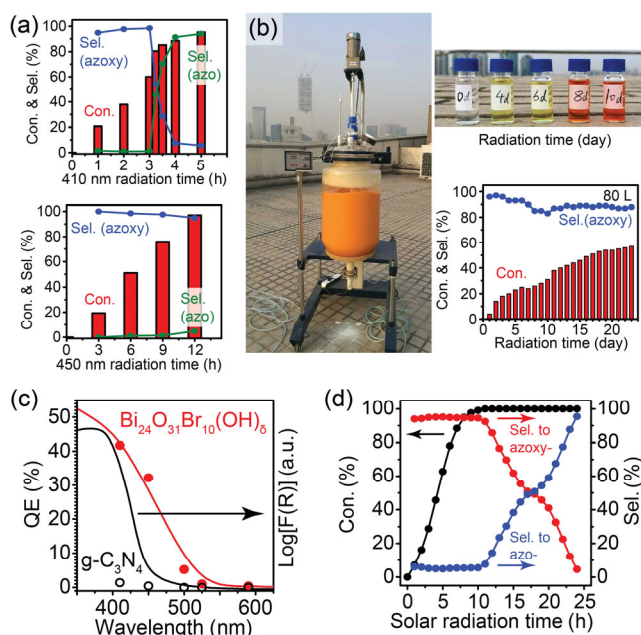


Figure 14 (a) The selective production of azoxybenzene and azobenzene over C_3N_4 photocatalyst by use of different light wavelengths. (b) The up-scaled photocatalytic system (80 L) under sunlight irradiation for azoxybenzene production. (Reprinted with permission from Ref. [42], © Dai, Y. T. et al. 2018) (c) The action spectra for bismuth oxybromide based photocatalyst in comparison with C_3N_4 . (d) The selective switch between azoxy- and azo-compounds under solar irradiation for different reaction time over $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}(\text{OH})_8$ photocatalyst. (Reprinted with permission from Ref. [43], © American Chemical Society 2018).

electrons can go to reduce nitro compounds to the desired azoxy- or azo-products. Very recently, the Su research group has successfully employed water as the hydrogen donor to realize the selective production of azoxybenzene under 410 nm irradiation with the production of H_2O_2 [130]. It indicates the type of hydrogen donors can significantly influence the selectivity of reduction products under visible light irradiation.

In addition, Dai et al. have further designed a bismuth oxybromide-based photocatalyst ($\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}(\text{OH})_8$) with basic sites on the surface for the selective reduction of nitroarenes [43]. This efficient photocatalyst was obtained via a microwave-assisted method, which quickly converts the suspension of *in-situ* formed bismuth oxybromide to the desired $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}(\text{OH})_8$ in the concentrated KOH solution (4 mol/L) within 4 min. The unique combination of photocatalysis with basic sites results in the promoted hydrogen transfer from isopropanol to the nitro group, presenting the highest quantum efficiencies (42% and 32% under 410 and 450 nm irradiation, respectively) in comparison with the above C_3N_4 system (Fig. 14(c)). More importantly, the selective switch between azoxy- and azo-products can be successfully realized in the 800 mL reaction system under solar irradiation for 2 days as shown in Fig. 14(d). The high yield of azoxybenzene (> 95%) is presented on the 1st day, while the full conversion of azoxybenzene to azobenzene appears on the 2nd day. This consecutive conversion of nitro compounds to azoxy-product and then to the azo one can be related to the strong adsorption of nitroarenes on the catalyst surface, whose hydroxyl sites make the main contribution. The thorough mechanism study reveals that after light irradiation the holes from bismuth based photocatalyst can efficiently convert isopropanol to acetone with the absence of a strong base

additive, while the following reduction step of nitro compounds by hydrogen species from alcohol oxidation and photoinduced electrons can be realized in the dark conditions.

Although the selective reductive coupling of nitroarenes to azoxy- or azo-compounds has been achieved via various photocatalysts, there exists one common problem in all photocatalytic systems. They fail to produce asymmetric azoxy/azo-aromatics with high selectivity. To this end, more efforts should be devoted to the design of novel photocatalysts with different reactive sites for surface redox reactions. One possible strategy is the integration between mild reduction of the nitro group and selective oxidation of the amino group in a single photocatalytic system. Each half-reaction can generate nitroso-arenes and hydroxylamines with different substituted groups, which finally participate in the N-N coupling reaction to selectively form asymmetric azoxy/azo-aromatics.

3.2.2 Alkyne hydrogenation

Selective semihydrogenation of alkynes is one kind of reduction organic transformation with vital importance, which can produce diverse useful alkenes for building natural products, pharmaceuticals and agrochemicals [131]. However, this selective hydrogenation is quite challenging since the semihydrogenation of triple bonds ($\text{C}\equiv\text{C}$) to double bonds ($\text{C}=\text{C}$) is difficult to proceed without overreduction to single bonds [132–134]. The photocatalytic hydrogen transfer strategy provides one efficient technique to realize the selective semihydrogenation of alkynes [135–143], which also avoids the employment of dangerous high-pressure H_2 and an external heat source. The basic idea of photocatalysis is to generate active hydrogen atoms on the surface of photocatalysts via the activation of hydrogen donors such as alcohols or water by holes and electrons [144, 145].

Except for the overhydrogenation towards alkanes, the photocatalytic evolution of H_2 as another competitive side reaction should be suppressed as well. Thus the controlled reconstruction of electronic structures or chemical states for too active metals (e.g., Pd and Pt) can be one feasible direction [146]. For example, the Xiong research group has fabricated PdPt alloy nanoparticles supported on TiO_2 , which can thoroughly regulate the binding strength between metal and H atoms (M–H) [136]. The $\text{Pd}_x\text{Pt}_{1-x}$ nanoparticles were successfully loaded on TiO_2 nanosheets via the reduction of K_2PdCl_4 and H_2PtCl_6 by use of a fresh NaBH_4 solution in a basic environment (pH = 9). The addition of different amounts of Pd and Pt salt precursor can well tune the Pd/Pt ratio in alloy nanoparticles. The M–H binding strength determines the movement of hydrogen atoms on the metal surface (e.g., adsorption, diffusion and desorption), which is crucial to the following semihydrogenation of alkynes. For the pure Pt nanoparticles, a significant amount of H_2 is produced with a relatively lower selectivity towards the alkene product (80%). The weaker Pt–H binding with a lower diffusion barrier also leads to the poor conversion of alkynes (50.5%) since hydrogen atoms are consumed for H_2 evolution. In contrast, the pure Pd case with a strong Pd–H binding can well suppress the production of H_2 to afford excellent selectivity for semihydrogenation (97%). However, the too strong M–H binding limits the transfer of hydrogen atoms to alkynes as well, thus hindering the conversion to 55%. As a combination design, the PdPt alloy photocatalyst ($\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{TiO}_2$) provides a perfect solution with moderate M–H binding, which results in almost full conversion of alkynes (99.6%) and high selectivity

to alkenes (94%) as shown in Fig. 15. The main photocatalytic cycle probably involves the photo-oxidation of alcohol molecules in water by TiO_2 under light irradiation in the first step, and then both the necessary electrons and hydrogen atoms abstracted from alcohols transfer to the surface of metal nanoparticles, which drive the addition of H atoms to unsaturated bonds (e.g., triple bonds) to produce the desired alkenes. In addition, it should be pointed out that the use of H_2 gas dramatically decreases the semihydrogenation selectivity to 64% because of high-level concentrations of dissociated hydrogen atoms on the metal surface.

Another successful strategy is to tailor the chemical states of active metals like Pt. The Wang research group has constructed two well-designed photocatalytic systems to reveal the vital role of Pt species in the selective semihydrogenation of phenylacetylene [141]. The oxidation state of Pt has been adjusted by the nanostructure of Nb_2O_5 support in this study. These supported photocatalysts were prepared via a sol-gel-calcination process. Briefly, ammonium niobate(V) oxalate, melamine and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ were mixed in ethanol to form a sol-gel precursor, which was dried by rotary evaporation and calcined in air to form $\text{Pt}/\text{Nb}_2\text{O}_5\text{-A}$ with a nanoplate morphology. Without the addition of melamine, it can produce the loading of Pt nanoparticles on bulky Nb_2O_5 as $\text{Pt}/\text{Nb}_2\text{O}_5$. Metallic Pt^0 dominates with bulky Nb_2O_5 as the support, while the positively charged $\text{Pt}^{\delta+}$ species appear in the case of two-dimensional (2D) Nb_2O_5 nanoplates. This support-mediation approach may originate from the available transport of oxygen atoms during the photocatalyst preparation process. CO-infrared spectroscopy, H_2 temperature-programmed reduction and X-ray photoelectron spectroscopy verify the formation of $\text{Pt}^{\delta+}\text{-O-Nb}$ structure. Thus the controlled regulation of Pt^0 towards $\text{Pt}^{\delta+}$ switches the main reduction product from H_2 to the desired styrene as shown in Fig. 16. This work emphasizes the vital importance of electronic and geometric structures of photocatalysts in alkyne hydrogenation. In addition, other co-catalysts such as Ag@Pd [142], Cu [135, 137] and Ni [143] nanoparticles have been well developed with high selectivity for the photocatalytic alkyne semihydrogenation. Specifically, in the case of $\text{Ni}/\text{C}_3\text{N}_4$, the control of selectivity is mainly enabled by the low affinity of alkene to the $\text{Ni}/\text{C}_3\text{N}_4$ composite

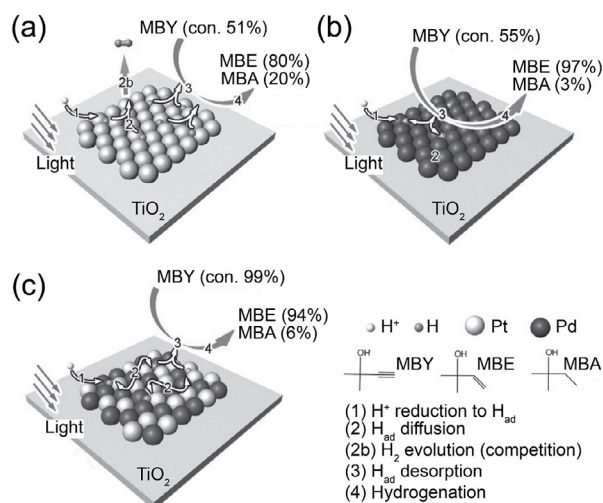


Figure 15 The photocatalytic hydrogen transfer and evolution processes at (a) Pt/TiO_2 ; (b) Pd/TiO_2 and (c) PdPt/TiO_2 . (Reproduced with permission from Ref. [136], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.

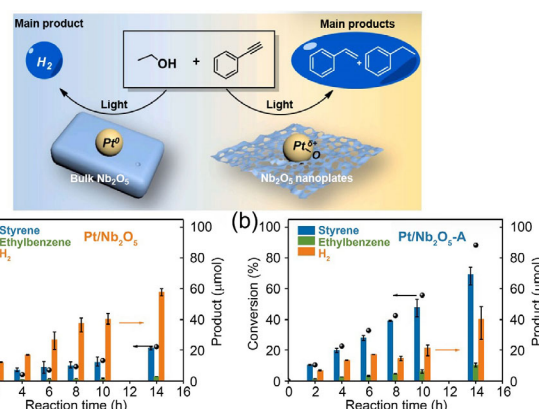


Figure 16 Time-dependent reaction performance of photocatalytic hydrogenation of phenylacetylene in the presence of (a) $\text{Pt}/\text{bulk Nb}_2\text{O}_5$ and (b) $\text{Pt}/\text{Nb}_2\text{O}_5\text{-A}$ nanoplates. (Adapted with permission from Ref. [141], © Elsevier B. V. 2021).

based on density functional theory calculations [143]. However, Ni species alone without C_3N_4 demonstrate a significantly higher affinity towards alkene, which could lead to undesired overhydrogenation. Despite the above-mentioned promising research progress, the regioselective semihydrogenation of diverse alkynes with the presence of other unsaturated groups (e.g., carbonyl and nitro group) is another research challenge for the design of next-generation heterogeneous photocatalysts. Tuning the adsorption/desorption of alkynes and alkenes and the diffusion/desorption of hydrogen atoms can make a big difference in the selectivity control of semihydrogenation reactions. Obviously, these key steps are closely related to the electronic/geometric structures and surface chemical micro-environment of heterogeneous photocatalysts.

3.2.3 C–O bond hydrogenolysis

Lignin is one of the three main constituents of lignocellulose, twisted closely by cellulose and hemicellulose to form robust cell walls in biomass. At present, roughly 50 million tons of lignin are generated from the pulp and paper industry every year, less than 2% of which can be recovered as a chemical product [147]. The phenylpropanol-based structures of lignin with high energy density render it serve as the renewable feedstock for the production of value-added aromatic chemicals [148]. As shown in Fig. 17, various C–O–C and C–C bonds randomly link the amorphous three-dimensional structure of lignin. To selectively convert lignin, several strategies have been explored, including acid-/alkali-promoted depolymerization [149, 150] and redox transformations [151]. However, the requirement of harsh reaction conditions (e.g., high temperature and pressure with high-level catalyst loadings) results in a significant amount of byproducts [152]. Among all the linkers, the $\beta\text{-O-4}$ linkage accounts for 40%–65% [153], whose cleavage has thus attracted much attention and extensive efforts. One promising technique via heterogeneous photocatalysis can achieve the selective cleavage of the $\text{C}_\beta\text{-O}$ bond in $\beta\text{-O-4}$ linker to promote the depolymerization of lignin under mild conditions [153–155].

Metal sulfides such as ZnIn_2S_4 and CdS -based photocatalysts have been extensively developed for the hydrogenolysis of $\text{C}_\beta\text{-O}$ bond. For example, in 2017 the Wang research group has prepared ZnIn_2S_4 nanoflowers with strong absorption in the visible region, whose absorption tail can reach ~ 550 nm with a bandgap of 2.16 eV [144]. The ZnIn_2S_4 nanoflowers

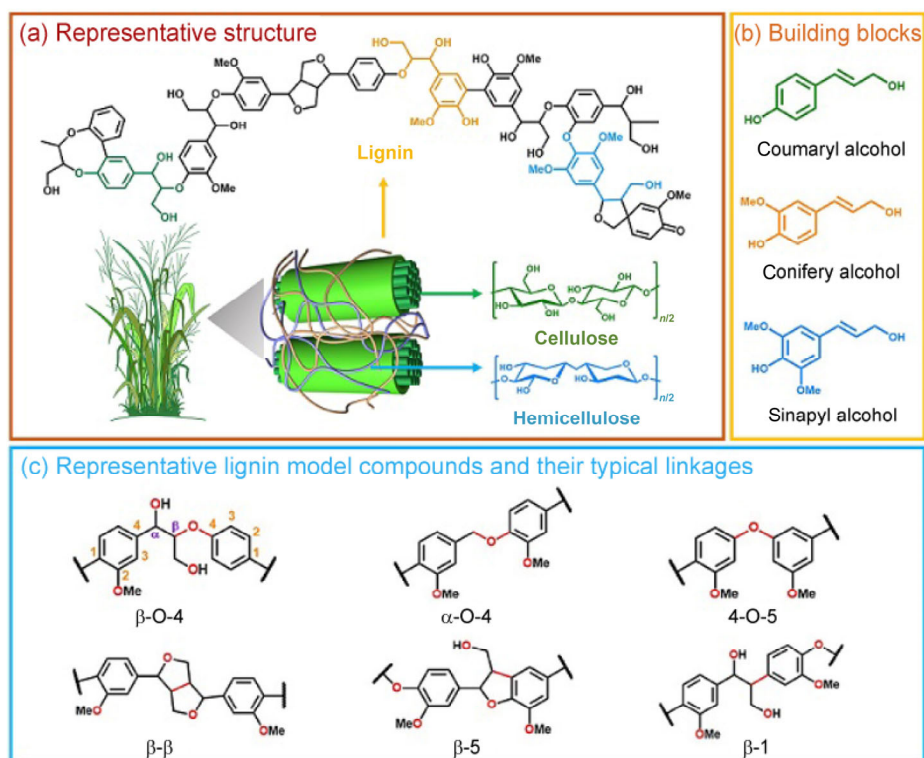


Figure 17 (a) The representative structure of lignin, cellulose and hemicellulose. (b) The building blocks for lignin. (c) The typical linkages in diverse lignin model compounds. (Reproduced with permission from Ref. [155], © Elsevier Ltd. 2021).

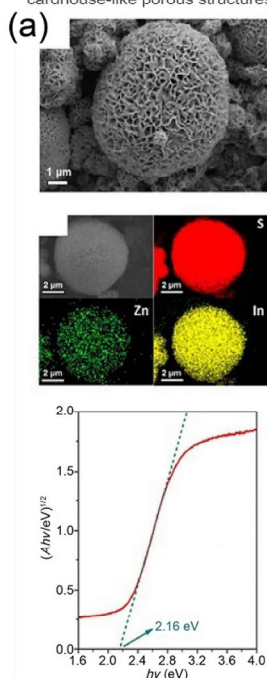
were prepared via a hydrothermal protocol, which employed $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ as metal precursors and cetyltrimethylammonium bromide (CTAB) as surfactants in the presence of a thioacetamide solution as the sulfur source. After 160 °C treatment for 16 h, the desired ZnIn_2S_4 photocatalyst can be obtained. As shown in Figs. 18(a)–18(c), a transfer hydrogenolysis method with an alcoholic group ($\text{C}_\alpha\text{H}-\text{OH}$) of lignin as the hydrogen source was reported, which is initially dehydrogenated with H atoms transfer to the surface of ZnIn_2S_4 to form a “hydrogen pool”. From the view of photocatalytic mechanisms, the holes from CBM located at 1.44 eV have the oxidative power to abstract H atoms from $\text{C}_\alpha\text{H}-\text{OH}$ group, leading to the generation of ketone intermediates. The combination of adsorbed protons with electrons is responsible for the formation of a “hydrogen pool”, which can selectively cleave the $\text{C}_\beta-\text{O}$ bond to produce two monomers. As a result, the active hydrogen species formed by the photoinduced holes and electrons are crucial to ensure the cleavage of β -O-4 linker. Moreover, the mild reaction conditions (temperature below 50 °C without the addition of strong acids or bases) efficiently suppress the recondensation of phenolic monomer products. Later, another research group has introduced a facile band engineering protocol by controlling the atomic ratio of Zn/In [156], offering a series of $\text{Zn}_m\text{In}_2\text{S}_{m+3}$ photocatalysts as displayed in Fig. 18(d). Among them, $\text{Zn}_4\text{In}_2\text{S}_7$ presents the highest performance for cleavage of β -O-4 bond with yields of 86% and 82% for ketone and phenol monomers, respectively. This can be ascribed to the effective tuning of band structures, coupling the suitable redox capability with sufficient visible-light absorption.

CdS-based photocatalysts present satisfactory photocatalytic performance towards the cleavage of the β -O-4 bond as well [157–160]. Especially, CdS quantum dots (QDs) with the size

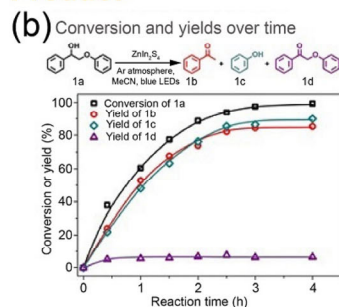
of 4.4 nm demonstrate the production of acetophenone and phenol in stoichiometric amounts with high yields (> 90%), four times higher than that of the nanoparticle counterpart [157]. CdS QDs were synthesized by a typical hot-injection approach, where a solution of sulfur in 1-octadecene (ODE) was rapidly injected into a hot mixture of CdO, ODE and oleic acid heated at 280 °C under argon atmosphere. It is mainly due to the increased bandgap with more powerful redox capability as shown in Fig. 19(a). The high selectivity is owed to the photoredox electro-hole coupled (EHCO) mechanism, where both holes and electrons involve the generation of monomer product from C_α radicals rather than the ketone intermediate (Fig. 19(b)). Initially, the susceptible $\text{C}_\alpha-\text{H}$ bonds experience the oxidative dehydrogenation of the model reactants by photogenerated holes to produce C_α radicals. Then the formed C_α radical can lead to the remarkably lower bond dissociation energy of the β -O-4 ether bond from 55 to 7.8 kcal/mol, which dramatically facilitates the desired reductive β -O-4 bond cleavage by the electrons. Therefore, the high selectivity and activity rely on the well-aligned photoredox system, which is specifically designed for the cleavage of β -O-4 linkages. Recently, other types of photocatalysts such as Ni/ZrO_2 [161], TiN [162] and C_3N_4 [163] have been employed to produce diverse valuable aromatics (e.g., styrene and aldehydes) from the reductive cleavage of C–O or even C–C bonds in different lignin models. Even though several efficient photocatalytic systems have been well developed with high selectivity for the hydrogenolysis of C–O bonds, there exist some challenges with respect to the efficiency, stability and selectivity over visible-light photocatalysts for more complicated reactants. Consequently, the development of superior photocatalysts should be focused on comprehensive regulation of band structures, morphologies and surface reactive

Catalyst

ZnIn₂S₄ nanosheets aggregate into cardhouse-like porous structures



Product



Mechanism

(c) Visible-light-driven self-hydrogen transfer hydrogenolysis (hydrogen pool)

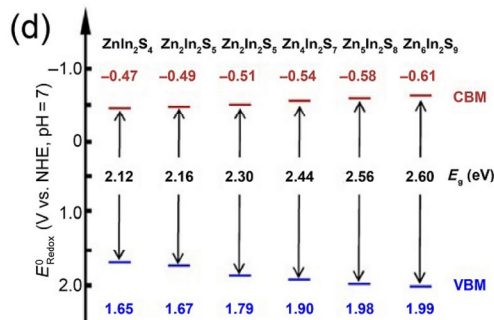
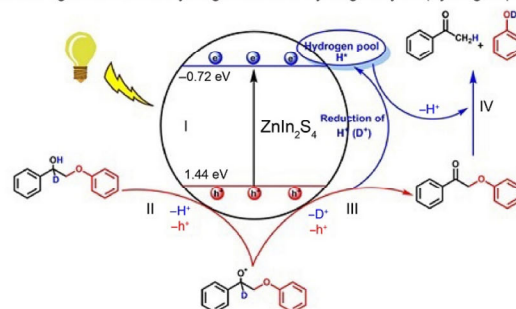


Figure 18 (a) SEM images of flower-like porous ZnIn₂S₄ with its light absorption profile. (b) Time-dependent photocatalytic performance for C–O bond cleavage. (c) The proposed mechanism for the self-hydrogen transfer hydrogenolysis over the ZnIn₂S₄ photocatalyst. (Reproduced with permission from Ref. [144], ©American Chemical Society 2017). (d) Band structures for a series of Zn_mIn_{2m+3} photocatalysts. (Adapted with permission from Ref. [156], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2019).

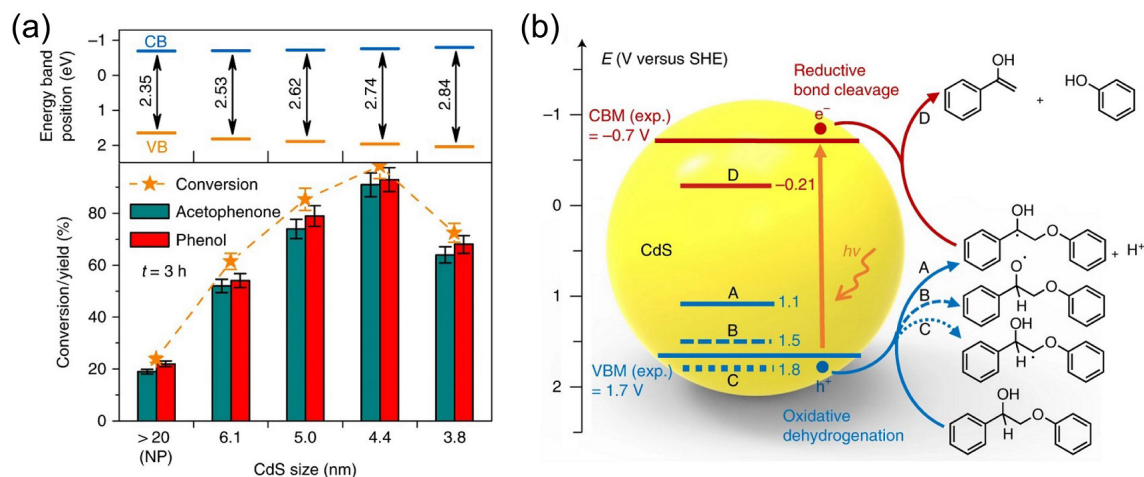


Figure 19 (a) Band structures and photocatalytic performance of CdS QDs with different sizes in contrast to nanoparticles. (b) The proposed EHCO mechanism for the photocatalytic hydrogenolysis of the lignin model over the CdS photocatalyst. (Reprinted with permission from Ref. [157], © Wu, X. J. et al. 2018).

sites, which can contribute to enhanced absorption of visible light, promoted charge separation/diffusion and controlled reaction paths.

4 Conclusions

Overall, several oxidative and reductive organic reactions have been well controlled via heterogeneous photocatalysis to produce the desired valuable compounds with high selectivity. To realize the precise control of selectivity, three key elements of heterogeneous photocatalysts have been thoroughly manipulated as follows.

(1) **Electronic structures.** The band structures can be well tuned by the elemental compositions of photocatalysts, such as doping with heteroatoms and forming heterojunctions. Even though a narrower bandgap can provide enhanced light absorption, the organic transformations can be prohibited if unaligned VBM/CBM positions are fabricated. The suitable redox power directly relates to the band structure of photocatalysts, whose VBM and CBM positions should cover the redox potentials of desired reactions in the thermodynamic aspect. For this reason, the redox capability of photocatalysts can be precisely regulated to exclude the useless side reactions that are usually triggered by too strong oxidative or reductive species.

(2) **Geometric structures.** The morphologies of photocatalyst materials not only influence the band structures due to the quantum confinement effect, but also alter the diffusion of photoinduced charge carriers and organic reactants/products. For example, the particle size of photocatalyst quantum dots can change the bandgap and VBM/CBM positions efficiently. The two-dimensional ultrathin nanosheets offer plenty of accessible active sites on the surface with highly under-coordinated states, which can create unique adsorption for organic molecules. It can consequently tune the reaction paths to promote the generation of desired products. Moreover, the diffusion path of holes/electrons can be shortened, suppressing the charge recombination. For supported photocatalysts, the chemical states of loaded metal nanoparticles also have a close relationship with the geometric structures of supports, which may present different interactions with the active metal species on the surface. Correspondingly, the selectivity of organic reactions can be tuned when the active metal species change their chemical states (e.g., from a metallic state to an oxidized one).

(3) **Surface chemical micro-environment.** The exposed metal species or local structures of photocatalysts directly participate in the adsorption/desorption and surface reaction of organic molecules. Thus one effective approach for selectivity control is to adjust the composition of metal species (e.g., alloys with different metal ratios). For the photocatalysts involving supported metal nanoparticles, the chemical properties of one metal substrate with too strong adsorption for certain reaction intermediates can be maneuvered by another incorporated metal. In this case, the suitable interaction with intermediate species (e.g., active hydrogen atoms) can ensure the occurrence of selective redox steps with controlled reaction rates to avoid any undesired overreaction. On the other hand, for metal-free photocatalysts such as polymeric materials, the local functional groups (e.g., hydroxyl or cyano) on the surface can tune the type of ROS (e.g., O_2^- , 1O_2 and $\cdot OH$), which significantly influence the oxidation degree. In parallel, the vacancy sites (e.g., O vacancies) and composition of co-catalysts (e.g., metal-chelate complexes) also regulate the selectivity via unique activation or energy transfer processes. Meanwhile, the co-existence of other functional sites (e.g., Lewis acid or basic sites) on the surface of photocatalysts can boost some specific reaction paths, which require the initiation by acidic or basic species.

Except for the above-mentioned factors from photocatalysts, the external reaction conditions, including reaction atmosphere (e.g., anaerobic or aerobic environment), light wavelength for irradiation, and solvent types (e.g., polar or nonpolar one), can serve as versatile knobs to control the selectivity of organic reactions as well. Given this situation, more careful investigations on the whole photocatalytic systems should be performed for better modulation of selectivity.

In the future, for the field of organic synthesis via heterogeneous photocatalysis more and more research focus may be located on two aspects in the view of reactions: (1) The existing challenging organic reactions. For example, the asymmetrical synthesis of azo/azoxy compounds requires a high selectivity control on asymmetry, which has not been realized by photocatalysis yet. Another important epoxidation of propene to propylene oxide is unable to be conducted with high selectivity in a photocatalytic system as well. In addition, some dehydrogenation reactions are quite important in the polymer industry, such as the direct dehydrogenation of ethylbenzene to styrene at 500–700 °C. However, a large

amount of heat energy is consumed during the dehydrogenation process. Are these significant dehydrogenation reactions possible to be realized in photocatalytic systems at room temperature with satisfactory yields? These kinds of meaningful reactions in the organic industry with the requirement of huge energy consumption (reaction temperature of ≥ 350 °C) or dangerous reaction conditions (e.g., high pressure of ≥ 5 MPa or the usage of H_2 gas bottle) can be ideal targets for heterogeneous photocatalysis. (2) The new organic reactions. This research direction is quite challenging but extremely exciting. The exploration will demand the effective integration of knowledge in the fields of organic chemistry, catalysis and solid materials. For instance, the direct insertion of a CO_2 molecule to n-pentane produces hexanoic acid. We expect that the design of novel reaction routes based on the catalytic properties of photocatalysts may provide a solution for some quite challenging organic syntheses, generating products with high regioselectivity or asymmetry.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

References

- [1] Taber, D. F. Oxidation and reduction in organic synthesis. In *Organic Synthesis: State of the Art 2005–2007*. Taber, D. F., Ed.; John Wiley & Sons, Inc.: Hoboken, 2008; pp 143–144.
- [2] Smith, M. B. Functional group exchange reactions: Oxidations. In *Organic Synthesis*. Smith, M. B., Ed.; 4th ed. Academic Press: Boston, 2017; pp 215–307.
- [3] Smith, M. B. Functional group exchange reactions: Reductions. In *Organic Synthesis*. Smith, M. B., Ed.; 4th ed. Academic Press: Boston, 2017; pp 309–418.
- [4] van Santen, R. A. Heterogeneous catalysis. In *Modern Heterogeneous Catalysis: An Introduction*. van Santen, R. A., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2017; pp 1–13.
- [5] Vogt, C.; Weckhuysen, B. M. The concept of active site in heterogeneous catalysis. *Nat. Rev. Chem.* **2022**, *6*, 89–111.
- [6] Guo, J.; Qin, Y. T.; Zhu, Y. F.; Zhang, X. F.; Long, C.; Zhao, M. T.; Tang, Z. Y. Metal-organic frameworks as catalytic selectivity regulators for organic transformations. *Chem. Soc. Rev.* **2021**, *50*, 5366–5396.
- [7] Grant, J. T.; Carrero, C. A.; Goeltl, F.; Venegas, J.; Mueller, P.; Burt, S. P.; Specht, S. E.; McDermott, W. P.; Chiericato, A.; Hermans, I. Selective oxidative dehydrogenation of propane to propene using boron nitride catalysts. *Science* **2016**, *354*, 1570–1573.
- [8] Lian, Z.; Si, C. W.; Jan, F.; Zhi, S. K.; Li, B. Coke deposition on Pt-based catalysts in propane direct dehydrogenation: Kinetics, suppression, and elimination. *ACS Catal.* **2021**, *11*, 9279–9292.
- [9] Zhang, Z. H.; Huber, G. W. Catalytic oxidation of carbohydrates into organic acids and furan chemicals. *Chem. Soc. Rev.* **2018**, *47*, 1351–1390.
- [10] Teong, S. P.; Yi, G. S.; Zhang, Y. G. Hydroxymethylfurfural production from bioresources: Past, present and future. *Green Chem.* **2014**, *16*, 2015–2026.

- [11] Rajendran, S.; Raghunathan, R.; Hevus, I.; Krishnan, R.; Ugrinov, A.; Sibi, M. P.; Webster, D. C.; Sivaguru, J. Programmed photodegradation of polymeric/oligomeric materials derived from renewable bioresources. *Angew. Chem., Int. Ed.* **2015**, *54*, 1159–1163.
- [12] Hopkins, K. T.; Wilson, W. D.; Bender, B. C.; McCurdy, D. R.; Hall, J. E.; Tidwell, R. R.; Kumar, A.; Bajic, M.; Boykin, D. W. Extended aromatic furan amidino derivatives as anti-*Pneumocystis carinii* agents. *J. Med. Chem.* **1998**, *41*, 3872–3878.
- [13] Braisted, A. C.; Oslob, J. D.; Delano, W. L.; Hyde, J.; McDowell, R. S.; Waal, N.; Yu, C.; Arkin, M. R.; Raimundo, B. C. Discovery of a potent small molecule IL-2 inhibitor through fragment assembly. *J. Am. Chem. Soc.* **2003**, *125*, 3714–3715.
- [14] Liu, H.; Cao, X. J.; Wei, J. N.; Jia, W. L.; Li, M. Z.; Tang, X.; Zeng, X. H.; Sun, Y.; Lei, T. Z.; Liu, S. J. et al. Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over Fe₂O₃-promoted MnO₂ catalyst. *ACS Sustainable Chem. Eng.* **2019**, *7*, 7812–7822.
- [15] Hirai, H. Oligomers from hydroxymethylfurancarboxylic acid. *J. Macromol. Sci.: Part A - Chem.* **1984**, *21*, 1165–1179.
- [16] Antonyraj, C. A.; Kim, B.; Kim, Y.; Shin, S.; Lee, K. Y.; Kim, I.; Cho, J. K. Heterogeneous selective oxidation of 5-hydroxymethyl-2-furfural (HMF) into 2,5-diformylfuran catalyzed by vanadium supported activated carbon in MIBK, extracting solvent for HMF. *Catal. Commun.* **2014**, *57*, 64–68.
- [17] Nie, J. F.; Xie, J. H.; Liu, H. C. Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on supported Ru catalysts. *J. Catal.* **2013**, *301*, 83–91.
- [18] Neatu, F.; Petrea, N.; Petre, R.; Somoghi, V.; Florea, M.; Parvulescu, V. I. Oxidation of 5-hydroxymethyl furfural to 2,5-diformylfuran in aqueous media over heterogeneous manganese based catalysts. *Catal. Today* **2016**, *278*, 66–73.
- [19] Siyo, B.; Schneider, M.; Radnik, J.; Pohl, M. M.; Langer, P.; Steinfeldt, N. Influence of support on the aerobic oxidation of HMF into FDCA over preformed Pd nanoparticle based materials. *Appl. Catal. A: Gen.* **2014**, *478*, 107–116.
- [20] Sahu, R.; Dhepe, P. L. Synthesis of 2,5-furandicarboxylic acid by the aerobic oxidation of 5-hydroxymethyl furfural over supported metal catalysts. *React. Kinet. Mech. Catal.* **2014**, *112*, 173–187.
- [21] Gorbanev, Y. Y.; Klitgaard, S. K.; Woodley, J. M.; Christensen, C. H.; Riisager, A. Gold-catalyzed aerobic oxidation of 5-hydroxymethylfurfural in water at ambient temperature. *ChemSusChem* **2009**, *2*, 672–675.
- [22] Salak Asghari, F.; Yoshida, H. Acid-catalyzed production of 5-hydroxymethyl furfural from d-fructose in subcritical water. *Ind. Eng. Chem. Res.* **2006**, *45*, 2163–2173.
- [23] Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. Reduction of nitro compounds using 3D-non-noble metal catalysts. *Chem. Rev.* **2019**, *119*, 2611–2680.
- [24] Zhao, J. X.; Chen, C. Q.; Xing, C. H.; Jiao, Z. F.; Yu, M. T.; Mei, B. B.; Yang, J.; Zhang, B. Y.; Jiang, Z.; Qin, Y. Selectivity regulation in Au-catalyzed nitroaromatic hydrogenation by anchoring single-site metal oxide promoters. *ACS Catal.* **2020**, *10*, 2837–2844.
- [25] Zhang, M.; Liu, Q.; Sun, L. B.; Su, H. J.; Qi, C. X. Synthesis of high efficient and stable Au@ZIF-8 with difference particle size for chemoselective hydrogenation of nitro compounds. *Catal. Lett.* **2020**, *150*, 438–449.
- [26] Bae, S.; Gim, S.; Kim, H.; Hanna, K. Effect of NaBH₄ on properties of nanoscale zero-valent iron and its catalytic activity for reduction of p-nitrophenol. *Appl. Catal. B: Environ.* **2016**, *182*, 541–549.
- [27] Moghaddam, M. M.; Pieber, B.; Glasnov, T.; Kappe, C. O. Immobilized iron oxide nanoparticles as stable and reusable catalysts for hydrazine-mediated nitro reductions in continuous flow. *ChemSusChem* **2014**, *7*, 3122–3131.
- [28] Jagadeesh, R. V.; Surkus, A. E.; Junge, H.; Pohl, M. M.; Radnik, J.; Rabeah, J.; Huan, H. M.; Schünemann, V.; Brückner, A.; Beller, M. Nanoscale Fe₂O₃-based catalysts for selective hydrogenation of nitroarenes to anilines. *Science* **2013**, *342*, 1073–1076.
- [29] Duan, Y. N.; Dong, X. S.; Song, T.; Wang, Z. Z.; Xiao, J. L.; Yuan, Y. Z.; Yang, Y. Hydrogenation of functionalized nitroarenes catalyzed by single-phase pyrite FeS₂ nanoparticles on N,S-codoped porous carbon. *ChemSusChem* **2019**, *12*, 4636–4644.
- [30] Thombal, P. R.; Rao, K. M.; Zo, S.; Narayanan, K. B.; Thombal, R. S.; Han, S. S. Efficient metal-free catalytic reduction of nitro to amine over carbon sheets doped with nitrogen. *Catal. Lett.* **2022**, *152*, 538–546.
- [31] Lang, X. J.; Chen, X. D.; Zhao, J. C. Heterogeneous visible light photocatalysis for selective organic transformations. *Chem. Soc. Rev.* **2014**, *43*, 473–486.
- [32] Schultz, D. M.; Yoon, T. P. Solar synthesis: Prospects in visible light photocatalysis. *Science* **2014**, *343*, 1239176.
- [33] Friedmann, D.; Hakki, A.; Kim, H.; Choi, W.; Bahnmann, D. Heterogeneous photocatalytic organic synthesis: State-of-the-art and future perspectives. *Green Chem.* **2016**, *18*, 5391–5411.
- [34] Luo, N. C.; Montini, T.; Zhang, J.; Fornasiero, P.; Fonda, E.; Hou, T. T.; Nie, W.; Lu, J. M.; Liu, J. X.; Heggen, M. et al. Visible-light-driven coproduction of diesel precursors and hydrogen from lignocellulose-derived methylfurans. *Nat. Energy* **2019**, *4*, 575–584.
- [35] Gisbertz, S.; Pieber, B. Heterogeneous Photocatalysis in Organic Synthesis. *ChemPhotoChem* **2020**, *4*, 456–475.
- [36] Filippini, G.; Longobardo, F.; Forster, L.; Criado, A.; Di Carmine, G.; Nasi, L.; D'Agostino, C.; Melchionna, M.; Fornasiero, P.; Prato, M. Light-driven, heterogeneous organocatalysts for C–C bond formation toward valuable perfluoroalkylated intermediates. *Sci. Adv.* **2020**, *6*, eabc9923.
- [37] Longobardo, F.; Gentile, G.; Criado, A.; Actis, A.; Colussi, S.; Dal Santo, V.; Chiesa, M.; Filippini, G.; Fornasiero, P.; Prato, M. et al. Tailored amorphization of graphitic carbon nitride triggers superior photocatalytic C–C coupling towards the synthesis of perfluoroalkyl derivatives. *Mater. Chem. Front.* **2021**, *5*, 7267–7275.
- [38] Lam, E.; Reisner, E. A TiO₂-Co(terpyridine)₂ photocatalyst for the selective oxidation of cellulose to formate coupled to the reduction of CO₂ to syngas. *Angew. Chem., Int. Ed.* **2021**, *60*, 23306–23312.
- [39] Rosso, C.; Filippini, G.; Criado, A.; Melchionna, M.; Fornasiero, P.; Prato, M. Metal-free photocatalysis: Two-dimensional nanomaterial connection toward advanced organic synthesis. *ACS Nano* **2021**, *15*, 3621–3630.
- [40] Cao, X.; Chen, Z.; Lin, R.; Cheong, W. C.; Liu, S. J.; Zhang, J.; Peng, Q.; Chen, C.; Han, T.; Tong, X. J. et al. A photochromic composite with enhanced carrier separation for the photocatalytic activation of benzylic C–H bonds in toluene. *Nat. Catal.* **2018**, *1*, 704–710.
- [41] Dai, Y. T.; Poidevin, C.; Ochoa-Hernández, C.; Auer, A. A.; Tüysüz, H. A supported bismuth halide perovskite photocatalyst for selective aliphatic and aromatic C–H bond activation. *Angew. Chem., Int. Ed.* **2020**, *59*, 5788–5796.
- [42] Dai, Y. T.; Li, C.; Shen, Y. B.; Lim, T.; Xu, J.; Li, Y. W.; Niemantsverdriet, H.; Besenbacher, F.; Lock, N.; Su, R. Light-tuned selective photosynthesis of azo- and azoxy-aromatics using graphitic C₃N₄. *Nat. Commun.* **2018**, *9*, 60.
- [43] Dai, Y. T.; Li, C.; Shen, Y. B.; Zhu, S. J.; Hvid, M. S.; Wu, L. C.; Skibsted, J.; Li, Y. W.; Niemantsverdriet, J. W. H.; Besenbacher, F. et al. Efficient solar-driven hydrogen transfer by bismuth-based photocatalyst with engineered basic sites. *J. Am. Chem. Soc.* **2018**, *140*, 16711–16719.
- [44] Li, X. B.; Xin, Z. K.; Xia, S. G.; Gao, X. Y.; Tung, C. H.; Wu, L. Z. Semiconductor nanocrystals for small molecule activation via artificial photosynthesis. *Chem. Soc. Rev.* **2020**, *49*, 9028–9056.
- [45] Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
- [46] Shi, X. F.; Zhang, J. H.; Cui, G. W.; Deng, N.; Wang, W.; Wang, Q.; Tang, B. Photocatalytic H₂ evolution improvement for H free-radical stabilization by electrostatic interaction of a Cu-BTC MOF with ZnO/GO. *Nano Res.* **2018**, *11*, 979–987.
- [47] Duan, J. Y.; Shi, W. D.; Xu, L. L.; Mou, G. Y.; Xin, Q. L.; Guan, J. G. Hierarchical nanostructures of fluorinated and naked Ta₂O₅ single crystalline nanorods: Hydrothermal preparation, formation mechanism and photocatalytic activity for H₂ production. *Chem. Commun.* **2012**, *48*, 7301–7303.

- [48] Wang, L. N.; Shi, X. Q.; Jia, Y. F.; Cheng, H. F.; Wang, L.; Wang, Q. Z. Recent advances in bismuth vanadate-based photocatalysts for photoelectrochemical water splitting. *Chin. Chem. Lett.* **2021**, *32*, 1869–1878.
- [49] Deng, C. H.; Ye, F.; Wang, T.; Ling, X. H.; Peng, L. L.; Yu, H.; Ding, K. Z.; Hu, H. M.; Dong, Q.; Le, H. R. et al. Developing hierarchical CdS/NiO hollow heterogeneous architectures for boosting photocatalytic hydrogen generation. *Nano Res.* **2022**, *15*, 2003–2012.
- [50] Wang, X. C.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* **2009**, *8*, 76–80.
- [51] Hara, M.; Hitoki, G.; Takata, T.; Kondo, J. N.; Kobayashi, H.; Domen, K. TaON and Ta₃N₅ as new visible light driven photocatalysts. *Catal. Today* **2003**, *78*, 555–560.
- [52] Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96.
- [53] Long, R.; Li, Y.; Song, L.; Xiong, Y. J. Coupling solar energy into reactions: Materials design for surface plasmon-mediated catalysis. *Small* **2015**, *11*, 3873–3889.
- [54] Ye, W.; Long, R.; Huang, H.; Xiong, Y. J. Plasmonic nanostructures in solar energy conversion. *J. Mater. Chem. C* **2017**, *5*, 1008–1021.
- [55] Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat. Mater.* **2011**, *10*, 911–921.
- [56] Chen, X.; Zhu, H. Y.; Zhao, J. C.; Zheng, Z. F.; Gao, X. P. Visible-light-driven oxidation of organic contaminants in air with gold nanoparticle catalysts on oxide supports. *Angew. Chem., Int. Ed.* **2008**, *47*, 5353–5356.
- [57] Wang, P.; Huang, B. B.; Qin, X. Y.; Zhang, X. Y.; Dai, Y.; Wei, J. Y.; Whangbo, M. H. Ag@AgCl: A highly efficient and stable photocatalyst active under visible light. *Angew. Chem., Int. Ed.* **2008**, *47*, 7931–7933.
- [58] Ahlawat, M.; Mittal, D.; Rao, V. G. Plasmon-induced hot-hole generation and extraction at nano-heterointerfaces for photocatalysis. *Commun. Mater.* **2021**, *2*, 114.
- [59] Li, J.; Lou, Z. Z.; Li, B. J. Nanostructured materials with localized surface plasmon resonance for photocatalysis. *Chin. Chem. Lett.* **2022**, *33*, 1154–1168.
- [60] Xiong, L. Q.; Tang, J. W. Strategies and challenges on selectivity of photocatalytic oxidation of organic substances. *Adv. Energy Mater.* **2021**, *11*, 2003216.
- [61] Valenzuela, M. A.; Albitzer, E.; Rios-Berny, O.; Córdova, I.; Flores, S. O. Photocatalytic reduction of organic compounds. *J. Adv. Oxid. Technol.* **2010**, *13*, 321–340.
- [62] Stroyuk, O. L.; Kuchmy, S. Y. Heterogeneous photocatalytic selective reductive transformations of organic compounds: A review. *Theor. Exp. Chem.* **2020**, *56*, 143–173.
- [63] Nosaka, Y.; Nosaka, A. Y. Generation and detection of reactive oxygen species in photocatalysis. *Chem. Rev.* **2017**, *117*, 11302–11336.
- [64] Sarina, S.; Zhu, H. Y.; Jaatinen, E.; Xiao, Q.; Liu, H. W.; Jia, J. F.; Chen, C.; Zhao, J. Enhancing catalytic performance of palladium in gold and palladium alloy nanoparticles for organic synthesis reactions through visible light irradiation at ambient temperatures. *J. Am. Chem. Soc.* **2013**, *135*, 5793–5801.
- [65] Wu, D.; Li, Z. Y.; Qi, Z. M.; Hu, S. W.; Long, R.; Song, L.; Xiong, Y. J. Boosting photocatalytic activity in cross-coupling reactions by constructing pd-oxide heterostructures. *ChemNanoMat* **2020**, *6*, 920–924.
- [66] Zhu, X. L.; Lin, Y. X.; Sun, Y.; Beard, M. C.; Yan, Y. Lead-halide perovskites for photocatalytic α -alkylation of aldehydes. *J. Am. Chem. Soc.* **2019**, *141*, 733–738.
- [67] Dai, Y. T.; Tüysüz, H. Lead-free Cs₃Bi₂Br₉ perovskite as photocatalyst for ring-opening reactions of epoxides. *ChemSusChem* **2019**, *12*, 2587–2592.
- [68] Duan, M. L.; Hu, C. Y.; Duan, D. L.; Chen, R. T.; Wang, C. M.; Wu, D.; Xia, T.; Liu, H. J.; Dai, Y. T.; Long, R. et al. ppm-level Cu dopant on ultrathin Pd nanosheets/TiO₂ for highly enhanced photocatalytic alcoholysis of epoxides. *Appl. Catal. B: Environ.* **2022**, *307*, 121211.
- [69] Zhao, Y. B.; Antonietti, M. Visible-light-irradiated graphitic carbon nitride photocatalyzed diels-alder reactions with dioxygen as sustainable mediator for photoinduced electrons. *Angew. Chem., Int. Ed.* **2017**, *56*, 9336–9340.
- [70] Huang, Z. P.; Zhao, Z. T.; Zhang, C. F.; Lu, J. M.; Liu, H. F.; Luo, N. C.; Zhang, J.; Wang, F. Enhanced photocatalytic alkane production from fatty acid decarboxylation via inhibition of radical oligomerization. *Nat. Catal.* **2020**, *3*, 170–178.
- [71] Han, Y. Z.; Huang, H.; Zhang, H. C.; Liu, Y.; Han, X.; Liu, R. H.; Li, H. T.; Kang, Z. H. Carbon quantum dots with photoenhanced hydrogen-bond catalytic activity in aldol condensations. *ACS Catal.* **2014**, *4*, 781–787.
- [72] Zhang, H.; Zhang, N.; Tang, Z. R.; Xu, Y. J. Transforming CdS into an efficient visible light photocatalyst for selective oxidation of saturated primary C–H bonds under ambient conditions. *Chem. Sci.* **2012**, *3*, 2812–2822.
- [73] Zhang, Z. Z.; Yang, Y. Y.; Wang, Y. Y.; Yang, L. L.; Li, Q.; Chen, L. X.; Xu, D. S. Revealing the A-site effect of lead-free A₃Sb₂Br₉ perovskite in photocatalytic C(sp³)-H bond activation. *Angew. Chem., Int. Ed.* **2020**, *59*, 18136–18139.
- [74] Guo, X. N.; Hao, C. H.; Jin, G. Q.; Zhu, H. Y.; Guo, X. Y. Copper nanoparticles on graphene support: An efficient photocatalyst for coupling of nitroaromatics in visible light. *Angew. Chem., Int. Ed.* **2014**, *53*, 1973–1977.
- [75] Wang, H.; Wang, L.; Zhang, J.; Wang, C. T.; Liu, Z. Y.; Gao, X. H.; Meng, X. J.; Yoo, S. J.; Kim, J. G.; Zhang, W. et al. Interfacial CoO_x layers on TiO₂ as an efficient catalyst for solvent-free aerobic oxidation of hydrocarbons. *ChemSusChem* **2018**, *11*, 3965–3974.
- [76] bin Saiman, M. I.; Brett, G. L.; Tiruvalam, R.; Forde, M. M.; Sharples, K.; Thetford, A.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Murphy, D. M. et al. Involvement of surface-bound radicals in the oxidation of toluene using supported Au-Pd nanoparticles. *Angew. Chem., Int. Ed.* **2012**, *51*, 5981–5985.
- [77] Yuan, R. S.; Fan, S. L.; Zhou, H. X.; Ding, Z. X.; Lin, S.; Li, Z. H.; Zhang, Z. Z.; Xu, C.; Wu, L.; Wang, X. X. et al. Chlorine-radical-mediated photocatalytic activation of C–H bonds with visible light. *Angew. Chem., Int. Ed.* **2013**, *52*, 1035–1039.
- [78] Liu, Y.; Chen, L.; Yuan, Q.; He, J.; Au, C. T.; Yin, S. F. A green and efficient photocatalytic route for the highly-selective oxidation of saturated alpha-carbon C–H bonds in aromatic alkanes over flower-like Bi₂WO₆. *Chem. Commun.* **2016**, *52*, 1274–1277.
- [79] Huang, H. W.; Yuan, H. F.; Zhao, J. W.; Solís-Fernández, G.; Zhou, C.; Seo, J. W.; Hendrix, J.; Debroye, E.; Steele, J. A.; Hofkens, J. et al. C(sp³)-H bond activation by perovskite solar photocatalyst cell. *ACS Energy Lett.* **2019**, *4*, 203–208.
- [80] Huang, Y.; Liu, C. B.; Li, M. Y.; Li, H. Z.; Li, Y. W.; Su, R.; Zhang, B. Photoimmobilized Ni clusters boost photodehydrogenative coupling of amines to imines via enhanced hydrogen evolution kinetics. *ACS Catal.* **2020**, *10*, 3904–3910.
- [81] Okunaka, S.; Tokudome, H.; Hitomi, Y. Selective oxidation of toluene to benzaldehyde over Pd/BiVO₄ particles under blue to green light irradiation. *J. Catal.* **2020**, *391*, 480–484.
- [82] Pahari, S. K.; Doong, R. A. Few-layered phosphorene-graphitic carbon nitride nanoheterostructure as a metal-free photocatalyst for aerobic oxidation of benzyl alcohol and toluene. *ACS Sustainable Chem. Eng.* **2020**, *8*, 13342–13351.
- [83] Dai, Y. T.; Tüysüz, H. Rapid acidic media growth of Cs₃Bi₂Br₉ halide perovskite platelets for photocatalytic toluene oxidation. *Sol. RRL* **2021**, *5*, 2100265.
- [84] Pahari, S. K.; Pal, P.; Srivastava, D. N.; Ghosh, S. C.; Panda, A. B. Efficient photocatalytic selective nitro-reduction and C–H bond oxidation over ultrathin sheet mediated CdS flowers. *Chem. Commun.* **2015**, *51*, 10322–10325.
- [85] Li, Z.; Zhang, M.; Xin, X.; Lv, H. J. Mechanistic studies on the photooxidation of 5-hydroxymethylfurfural by polyoxometalate catalysts and atmospheric oxygen. *ChemCatChem* **2021**, *13*, 1389–1395.

- [86] Li, C. C.; Na, Y. Recent advances in photocatalytic oxidation of 5-hydroxymethylfurfural. *ChemPhotoChem* **2021**, *5*, 502–511.
- [87] Xu, S.; Zhou, P.; Zhang, Z. H.; Yang, C. J.; Zhang, B. G.; Deng, K. J.; Bottle, S.; Zhu, H. Y. Selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid using O₂ and a photocatalyst of Co-thiophopyrazine bonded to g-C₃N₄. *J. Am. Chem. Soc.* **2017**, *139*, 14775–14782.
- [88] Iqbal, N.; Choi, S.; You, Y. M.; Cho, E. J. Aerobic oxidation of aldehydes by visible light photocatalysis. *Tetrahedron Lett.* **2013**, *54*, 6222–6225.
- [89] Chen, Y. Z.; Wang, Z. U.; Wang, H. W.; Lu, J. L.; Yu, S. H.; Jiang, H. L. Singlet oxygen-engaged selective photo-oxidation over Pt nanocrystals/porphyrinic MOF: The roles of photothermal effect and Pt electronic state. *J. Am. Chem. Soc.* **2017**, *139*, 2035–2044.
- [90] Khan, A.; Goepel, M.; Kubas, A.; Lomot, D.; Lisowski, W.; Lisovyt'skiy, D.; Nowicka, A.; Colmenares, J. C.; Gläser, R. Selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran by visible light-driven photocatalysis over *in situ* substrate-sensitized titania. *ChemSusChem* **2021**, *14*, 1351–1362.
- [91] Xue, J. J.; Huang, C. J.; Zong, Y. Q.; Gu, J. D.; Wang, M. X.; Ma, S. Fe(III)-grafted Bi₂MoO₆ nanoplates for enhanced photocatalytic activities on tetracycline degradation and HMF oxidation. *Appl. Organomet. Chem.* **2019**, *33*, e5187.
- [92] DiMeglio, J. L.; Breuhaus-Alvarez, A. G.; Li, S. Q.; Bartlett, B. M. Nitrate-mediated alcohol oxidation on cadmium sulfide photocatalysts. *ACS Catal.* **2019**, *9*, 5732–5741.
- [93] Zhou, B. W.; Song, J. L.; Zhang, Z. R.; Jiang, Z. W.; Zhang, P.; Han, B. X. Highly selective photocatalytic oxidation of biomass-derived chemicals to carboxyl compounds over Au/TiO₂. *Green Chem.* **2017**, *19*, 1075–1081.
- [94] Zhang, W. Z.; Li, X. X.; Liu, S. R.; Qiu, J. H.; An, J. H.; Yao, J. F.; Zuo, S. L.; Zhang, B.; Xia, H. A.; Li, C. Z. Photocatalytic oxidation of 5-hydroxymethylfurfural over interfacial-enhanced Ag/TiO₂ under visible light irradiation. *ChemSusChem*, in press, <http://doi.org/10.1002/cssc.202102158>.
- [95] Ma, B.; Wang, Y. Y.; Guo, X. N.; Tong, X. L.; Liu, C.; Wang, Y. W.; Guo, X. Y. Photocatalytic synthesis of 2,5-diformylfuran from 5-hydroxymethylfurfural or fructose over bimetallic Au-Ru nanoparticles supported on reduced graphene oxides. *Appl. Catal. A: Gen.* **2018**, *552*, 70–76.
- [96] Ilkaeva, M.; Krivtsov, I.; García-López, E. I.; Marci, G.; Khainakova, O.; García, J. R.; Palmisano, L.; Díaz, E.; Ordóñez, S. Selective photocatalytic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxaldehyde by polymeric carbon nitride-hydrogen peroxide adduct. *J. Catal.* **2018**, *359*, 212–222.
- [97] Zhu, Y. K.; Zhang, Y.; Cheng, L. L.; Ismael, M.; Feng, Z. Y.; Wu, Y. Novel application of g-C₃N₄/NaNbO₃ composite for photocatalytic selective oxidation of biomass-derived HMF to FFCA under visible light irradiation. *Adv. Powder Technol.* **2020**, *31*, 1148–1159.
- [98] Ayed, C.; Huang, W.; Kizilsavas, G.; Landfester, K.; Zhang, K. A. I. Photocatalytic partial oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) over a covalent triazine framework in water. *ChemPhotoChem* **2020**, *4*, 571–576.
- [99] Zhang, M.; Li, Z.; Xin, X.; Zhang, J. H.; Feng, Y. Q.; Lv, H. J. Selective valorization of 5-hydroxymethylfurfural to 2,5-diformylfuran using atmospheric O₂ and MAPbBr₃ perovskite under visible light. *ACS Catal.* **2020**, *10*, 14793–14800.
- [100] Wan, X. Y.; Zhou, C. M.; Chen, J. S.; Deng, W. P.; Zhang, Q. H.; Yang, Y. H.; Wang, Y. Base-free aerobic oxidation of 5-hydroxymethyl-furfural to 2,5-furandicarboxylic acid in water catalyzed by functionalized carbon nanotube-supported Au-Pd alloy nanoparticles. *ACS Catal.* **2014**, *4*, 2175–2185.
- [101] Sharma, A. S.; Sharma, V. S.; Kaur, H.; Varma, R. S. Supported heterogeneous nanocatalysts in sustainable, selective and eco-friendly epoxidation of olefins. *Green Chem.* **2020**, *22*, 5902–5936.
- [102] BCC Research LLC. *CHM102A Olefin Derivatives: Global Markets to 2022*, 2018. <https://www.bccresearch.com/market-research/chemicals/olefin-derivatives-global-markets.html> (accessed April 11 2022)
- [103] Sienel, G.; Rieth, R.; Rowbottom, K. T. Epoxides. In *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000.
- [104] Lin, M.; Xia, C. J.; Zhu, B.; Li, H.; Shu, X. T. Green and efficient epoxidation of propylene with hydrogen peroxide (HPPO process) catalyzed by hollow TS-1 zeolite: A 1.0 kt/a pilot-scale study. *Chem. Eng. J.* **2016**, *295*, 370–375.
- [105] Khatib, S. J.; Oyama, S. T. Direct oxidation of propylene to propylene oxide with molecular oxygen: A review. *Catal. Rev.* **2015**, *57*, 306–344.
- [106] Teržan, J.; Huš, M.; Likozar, B.; Djinović, P. Propylene epoxidation using molecular oxygen over copper- and silver-based catalysts: A review. *ACS Catal.* **2020**, *10*, 13415–13436.
- [107] Ohno, T.; Masaki, Y.; Hirayama, S.; Matsumura, M. TiO₂-photocatalyzed epoxidation of 1-decene by H₂O₂ under visible light. *J. Catal.* **2001**, *204*, 163–168.
- [108] Huang, Y. M.; Liu, Z.; Gao, G. P.; Xiao, G.; Du, A. J.; Bottle, S.; Sarina, S.; Zhu, H. Y. Stable copper nanoparticle photocatalysts for selective epoxidation of alkenes with visible light. *ACS Catal.* **2017**, *7*, 4975–4985.
- [109] Marimuthu, A.; Zhang, J. W.; Linic, S. Tuning selectivity in propylene epoxidation by plasmon mediated photo-switching of Cu oxidation state. *Science* **2013**, *339*, 1590–1593.
- [110] Hosseini-Sarvari, M.; Bazayr, Z. Selective visible-light photocatalytic aerobic oxidation of alkenes to epoxides with Pd/ZnO nanoparticles. *ChemistrySelect* **2020**, *5*, 8853–8857.
- [111] Weerathunga, H.; Brock, A. J.; Sarina, S.; Deshan, A. D. K.; Zhu, H. Y.; Waclawik, E. R. AuCu/ZnO heterogeneous photocatalysts: Photodeposited AuCu alloy effect on product selectivity in alkene epoxidation. *J. Photochem. Photobiol. A: Chem.* **2022**, *426*, 113732.
- [112] Tan, H.; Kong, P.; Zhang, R. G.; Gao, M. T.; Liu, M. X.; Gu, X. M.; Liu, W. F.; Zheng, Z. F. Controllable generation of reactive oxygen species on cyano-group-modified carbon nitride for selective epoxidation of styrene. *Innovation* **2021**, *2*, 100089.
- [113] Gu, Q.; Jiang, P. P.; Shen, Y. R.; Zhang, K.; Wai, P. T.; Haryono, A. Lamellar porous Mo-modified carbon nitride polymers photocatalytic epoxidation of olefins. *Mol. Catal.* **2021**, *504*, 111441.
- [114] Li, M.; Ma, L. N.; Luo, L.; Liu, Y. G.; Xu, M.; Zhou, H.; Wang, Y.; Li, Z. H.; Kong, X. G.; Duan, H. H. Efficient photocatalytic epoxidation of styrene over a quantum-sized SnO₂ on carbon nitride as a heterostructured catalyst. *Appl. Catal. B: Environ.* **2022**, *309*, 121268.
- [115] Földner, S.; Mild, R.; Siegmund, H. I.; Schroeder, J. A.; Gruber, M.; König, B. Green-light photocatalytic reduction using dye-sensitized TiO₂ and transition metal nanoparticles. *Green Chem.* **2010**, *12*, 400–406.
- [116] Shiraishi, Y.; Togawa, Y.; Tsukamoto, D.; Tanaka, S.; Hirai, T. Highly efficient and selective hydrogenation of nitroaromatics on photoactivated rutile titanium dioxide. *ACS Catal.* **2012**, *2*, 2475–2481.
- [117] Liu, L. C.; Gu, X. R.; Ji, Z. Y.; Zou, W. X.; Tang, C. J.; Gao, F.; Dong, L. Anion-assisted synthesis of TiO₂ nanocrystals with tunable crystal forms and crystal facets and their photocatalytic redox activities in organic reactions. *J. Phys. Chem. C* **2013**, *117*, 18578–18587.
- [118] Shiraishi, Y.; Hirakawa, H.; Togawa, Y.; Sugano, Y.; Ichikawa, S.; Hirai, T. Rutile crystallites isolated from degussa (Evonik) P25 TiO₂: Highly efficient photocatalyst for chemoselective hydrogenation of nitroaromatics. *ACS Catal.* **2013**, *3*, 2318–2326.
- [119] Chen, Z.; Liu, S. Q.; Yang, M. Q.; Xu, Y. J. Synthesis of uniform CdS nanospheres/graphene hybrid nanocomposites and their application as visible light photocatalyst for selective reduction of nitro organics in water. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4309–4319.
- [120] Eskandari, P.; Kazemi, F.; Zand, Z. Photocatalytic reduction of aromatic nitro compounds using CdS nanostructure under blue LED irradiation. *J. Photochem. Photobiol. A: Chem.* **2014**, *274*, 7–12.
- [121] Gao, W. Z.; Xu, Y.; Chen, Y.; Fu, W. F. Highly efficient and selective photocatalytic reduction of nitroarenes using the Ni₂P/CdS

- catalyst under visible-light irradiation. *Chem. Commun.* **2015**, *51*, 13217–13220.
- [122] Toyao, T.; Saito, M.; Horiuchi, Y.; Mochizuki, K.; Iwata, M.; Higashimura, H.; Matsuoka, M. Efficient hydrogen production and photocatalytic reduction of nitrobenzene over a visible-light-responsive metal-organic framework photocatalyst. *Catal. Sci. Technol.* **2013**, *3*, 2092–2097.
- [123] Wu, W. M.; Lin, R.; Shen, L. J.; Liang, R. W.; Yuan, R. S.; Wu, L. Highly efficient visible-light-induced photocatalytic hydrogenation of nitrobenzene to aniline in water. *RSC Adv.* **2013**, *3*, 10894–10899.
- [124] Zhu, H. Y.; Ke, X. B.; Yang, X. Z.; Sarina, S.; Liu, H. W. Reduction of nitroaromatic compounds on supported gold nanoparticles by visible and ultraviolet light. *Angew. Chem., Int. Ed.* **2010**, *49*, 9657–9661.
- [125] Ke, X. B.; Zhang, X. G.; Zhao, J.; Sarina, S.; Barry, J.; Zhu, H. Y. Selective reductions using visible light photocatalysts of supported gold nanoparticles. *Green Chem.* **2013**, *15*, 236–244.
- [126] Naya, S. I.; Niwa, T.; Kume, T.; Tada, H. Visible-light-induced electron transport from small to large nanoparticles in bimodal gold nanoparticle-loaded titanium(IV) oxide. *Angew. Chem., Int. Ed.* **2014**, *53*, 7305–7309.
- [127] Mondal, B.; Mukherjee, P. S. Cage encapsulated gold nanoparticles as heterogeneous photocatalyst for facile and selective reduction of nitroarenes to Azo compounds. *J. Am. Chem. Soc.* **2018**, *140*, 12592–12601.
- [128] Xiao, Q.; Liu, Z.; Wang, F.; Sarina, S.; Zhu, H. Y. Tuning the reduction power of visible-light photocatalysts of gold nanoparticles for selective reduction of nitroaromatics to azoxy-compounds—Tailoring the catalyst support. *Appl. Catal. B: Environ.* **2017**, *209*, 69–79.
- [129] Liu, Z.; Huang, Y. M.; Xiao, Q.; Zhu, H. Y. Selective reduction of nitroaromatics to azoxy compounds on supported Ag-Cu alloy nanoparticles through visible light irradiation. *Green Chem.* **2016**, *18*, 817–825.
- [130] Zhang, D. S.; Ren, P. J.; Liu, W. W.; Li, Y. R.; Salli, S.; Han, F. Y.; Qiao, W.; Liu, Y.; Fan, Y. Z.; Cui, Y. et al. Photocatalytic abstraction of hydrogen atoms from water using hydroxylated graphitic carbon nitride for hydrogenative coupling reactions. *Angew. Chem., Int. Ed.*, in press, <https://doi.org/10.1002/anie.202204256>.
- [131] Oger, C.; Balas, L.; Durand, T.; Galano, J. M. Are alkyne reductions chemo-, regio-, and stereoselective enough to provide pure (Z)-olefins in polyfunctionalized bioactive molecules?. *Chem. Rev.* **2013**, *113*, 1313–1350.
- [132] Feng, Q. C.; Zhao, S.; Wang, Y.; Dong, J. C.; Chen, W. X.; He, D. S.; Wang, D. S.; Yang, J.; Zhu, Y. M.; Zhu, H. L. et al. Isolated single-atom Pd sites in intermetallic nanostructures: High catalytic selectivity for semihydrogenation of alkynes. *J. Am. Chem. Soc.* **2017**, *139*, 7294–7301.
- [133] Zhao, X. J.; Zhou, L. Y.; Zhang, W. Y.; Hu, C. Y.; Dai, L.; Ren, L. T.; Wu, B. H.; Fu, G.; Zheng, N. F. Thiol treatment creates selective palladium catalysts for semihydrogenation of internal alkynes. *Chem* **2018**, *4*, 1080–1091.
- [134] Wang, S.; Zhao, Z. J.; Chang, X.; Zhao, J. B.; Tian, H.; Yang, C. S.; Li, M. R.; Fu, Q.; Mu, R. T.; Gong, J. L. Activation and spillover of hydrogen on sub-1 nm palladium nanoclusters confined within sodalite zeolite for the semi-hydrogenation of alkynes. *Angew. Chem., Int. Ed.* **2019**, *58*, 7668–7672.
- [135] Kominami, H.; Higa, M.; Nojima, T.; Ito, T.; Nakanishi, K.; Hashimoto, K.; Imamura, K. Copper-modified titanium dioxide: A simple photocatalyst for the chemoselective and diastereoselective hydrogenation of alkynes to alkenes under additive-free conditions. *ChemCatChem* **2016**, *8*, 2019–2022.
- [136] Li, M. Q.; Zhang, N.; Long, R.; Ye, W.; Wang, C. M.; Xiong, Y. J. PdPt alloy nanocatalysts supported on TiO₂: Maneuvering metal-hydrogen interactions for light-driven and water-donating selective alkyne semihydrogenation. *Small* **2017**, *13*, 1604173.
- [137] Kominami, H.; Shiba, M.; Hashimoto, A.; Imai, S.; Nakanishi, K.; Tanaka, A.; Hashimoto, K.; Imamura, K. Titanium(IV) oxide having a copper co-catalyst: A new type of semihydrogenation photocatalyst working efficiently at an elevated temperature under hydrogen-free and poison-free conditions. *Phys. Chem. Chem. Phys.* **2018**, *20*, 19321–19325.
- [138] Kojima, Y.; Fukui, M.; Tanaka, A.; Hashimoto, K.; Kominami, H. Additive-free semihydrogenation of an alkynyl group to an alkenyl group over Pd-TiO₂ photocatalyst utilizing temporary *in-situ* deactivation. *ChemCatChem* **2018**, *10*, 3605–3611.
- [139] Fukui, M.; Omori, Y.; Kitagawa, S. Y.; Tanaka, A.; Hashimoto, K.; Kominami, H. Visible light-induced diastereoselective semihydrogenation of alkynes to cis-alkenes over an organically modified titanium(IV) oxide photocatalyst having a metal co-catalyst. *J. Catal.* **2019**, *374*, 36–42.
- [140] Lian, J. H.; Chai, Y. C.; Qi, Y.; Guo, X. Y.; Guan, N. J.; Li, L. D.; Zhang, F. X. Unexpectedly selective hydrogenation of phenylacetylene to styrene on titania supported platinum photocatalyst under 385 nm monochromatic light irradiation. *Chin. J. Catal.* **2020**, *41*, 598–603.
- [141] Su, K. Y.; Wang, Y. H.; Zhang, C. F.; Gao, Z. Y.; Han, J. Y.; Wang, F. Tuning the Pt species on Nb₂O₅ by support-induced modification in the photocatalytic transfer hydrogenation of phenylacetylene. *Appl. Catal. B: Environ.* **2021**, *298*, 120554.
- [142] Imai, S.; Kojima, Y.; Fudo, E.; Tanaka, A.; Kominami, H. Controlling the performance of a silver co-catalyst by a palladium core in TiO₂-photocatalyzed alkyne semihydrogenation and H₂ production. *Appl. Catal. A: Gen.* **2021**, *624*, 118331.
- [143] Jia, T. T.; Meng, D.; Ji, H. W.; Sheng, H.; Chen, C. C.; Song, W. J.; Zhao, J. C. Visible-light-driven semihydrogenation of alkynes via proton reduction over carbon nitride supported nickel. *Appl. Catal. B: Environ.* **2022**, *304*, 121004.
- [144] Luo, N. C.; Wang, M.; Li, H. J.; Zhang, J.; Hou, T. T.; Chen, H. J.; Zhang, X. C.; Lu, J. M.; Wang, F. Visible-light-driven self-hydrogen transfer hydrogenolysis of lignin models and extracts into phenolic products. *ACS Catal.* **2017**, *7*, 4571–4580.
- [145] Li, H. J.; Gao, Z. Y.; Lei, L. J.; Liu, H. F.; Han, J. Y.; Hong, F.; Luo, N. C.; Wang, F. Photocatalytic transfer hydrogenolysis of aromatic ketones using alcohols. *Green Chem.* **2020**, *22*, 3802–3808.
- [146] Shen, C. Q.; Ji, Y. J.; Wang, P. T.; Bai, S. X.; Wang, M.; Li, Y. Y.; Huang, X. Q.; Shao, Q. Interface confinement in metal nanosheet for high-efficiency semi-hydrogenation of alkynes. *ACS Catal.* **2021**, *11*, 5231–5239.
- [147] Sun, Z. H.; Fridrich, B.; de Santi, A.; Elangovan, S.; Barta, K. Bright side of lignin depolymerization: Toward new platform chemicals. *Chem. Rev.* **2018**, *118*, 614–678.
- [148] Liao, Y. H.; Koelewijn, S. F.; Van den Bossche, G.; Van Aelst, J.; Van den Bosch, S.; Renders, T.; Navare, K.; Nicolai, T.; Van Aelst, K.; Maesen, M. et al. A sustainable wood biorefinery for low-carbon footprint chemicals production. *Science* **2020**, *367*, 1385–1390.
- [149] Wang, H. L.; Ruan, H.; Feng, M. Q.; Qin, Y. L.; Job, H.; Luo, L. L.; Wang, C. M.; Engelhard, M. H.; Kuhn, E.; Chen, X. W. et al. One-pot process for hydrodeoxygenation of lignin to alkanes using Ru-based bimetallic and bifunctional catalysts supported on Zeolite Y. *ChemSusChem* **2017**, *10*, 1846–1856.
- [150] Schutyser, W.; Kruger, J. S.; Robinson, A. M.; Katahira, R.; Brandner, D. G.; Cleveland, N. S.; Mittal, A.; Peterson, D. J.; Meilan, R.; Román-Leshkov, Y. et al. Revisiting alkaline aerobic lignin oxidation. *Green Chem.* **2018**, *20*, 3828–3844.
- [151] Wang, H. L.; Ruan, H.; Pei, H. S.; Wang, H. M.; Chen, X. W.; Tucker, M. P.; Cort, J. R.; Yang, B. Biomass-derived lignin to jet fuel range hydrocarbons via aqueous phase hydrodeoxygenation. *Green Chem.* **2015**, *17*, 5131–5135.
- [152] Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S. F.; Beckham, G. T.; Sels, B. F. Chemicals from lignin: An interplay of lignocellulose fractionation, depolymerisation, and upgrading. *Chem. Soc. Rev.* **2018**, *47*, 852–908.
- [153] Zhang, C. F.; Wang, F. Catalytic lignin depolymerization to aromatic chemicals. *Acc. Chem. Res.* **2020**, *53*, 470–484.
- [154] Xiang, Z. Y.; Han, W. Y.; Deng, J.; Zhu, W. B.; Zhang, Y.; Wang, H. J. Photocatalytic conversion of lignin into chemicals and fuels. *ChemSusChem* **2020**, *13*, 4199–4213.
- [155] Chen, H.; Wan, K.; Zheng, F. J.; Zhang, Z.; Zhang, Y. Y.; Long, D. H. Mechanism insight into photocatalytic conversion of lignin for

- valuable chemicals and fuels production: A state-of-the-art review. *Renewable Sustainable Energy Rev.* **2021**, *147*, 111217.
- [156] Lin, J. C.; Wu, X. J.; Xie, S. J.; Chen, L. Y.; Zhang, Q. H.; Deng, W. P.; Wang, Y. Visible-light-driven cleavage of C-O linkage for lignin valorization to functionalized aromatics. *ChemSusChem* **2019**, *12*, 5023–5031.
- [157] Wu, X. J.; Fan, X. T.; Xie, S. J.; Lin, J. C.; Cheng, J.; Zhang, Q. H.; Chen, L. Y.; Wang, Y. Solar energy-driven lignin-first approach to full utilization of lignocellulosic biomass under mild conditions. *Nat. Catal.* **2018**, *1*, 772–780.
- [158] Wu, X. J.; Xie, S. J.; Liu, C. X.; Zhou, C.; Lin, J. C.; Kang, J. C.; Zhang, Q. H.; Wang, Z. H.; Wang, Y. Ligand-controlled photocatalysis of CdS quantum dots for lignin valorization under visible light. *ACS Catal.* **2019**, *9*, 8443–8451.
- [159] Han, G. Q.; Yan, T.; Zhang, W.; Zhang, Y. C.; Lee, D. Y.; Cao, Z.; Sun, Y. J. Highly selective photocatalytic valorization of lignin model compounds using ultrathin metal/CdS. *ACS Catal.* **2019**, *9*, 11341–11349.
- [160] Yoo, H.; Lee, M. W.; Lee, S.; Lee, J.; Cho, S.; Lee, H.; Cha, H. G.; Kim, H. S. Enhancing photocatalytic β -O-4 bond cleavage in lignin model compounds by silver-exchanged cadmium sulfide. *ACS Catal.* **2020**, *10*, 8465–8475.
- [161] Li, P. F.; Ouyang, Y. X.; Xiao, G.; Zhao, Y. L.; Sarina, S.; Baeyens, J.; Su, H. J.; Zhu, H. Y. Non-plasmonic Ni nanoparticles catalyzed visible light selective hydrogenolysis of aryl ethers in lignin under mild conditions. *Green Chem.* **2021**, *23*, 7780–7789.
- [162] Liu, Z.; Huang, Y. M.; Xiao, G.; Li, P. F.; Su, H. J.; Sarina, S.; Zhu, H. Y. Visible-light-driven efficient cleavage of β -O-4 linkage in a lignin model compound: Phenethyl phenyl ether photocatalyzed by titanium nitride nanoparticles. *Energy Fuels* **2021**, *35*, 13315–13324.
- [163] Ku, C. H.; Guo, H. Q.; Li, K. X.; Wu, Q.; Yan, L. S. One-step fabrication of mesoporous sulfur-doped carbon nitride for highly selective photocatalytic transformation of native lignin to monophenolic compounds. *Chin. Chem. Lett.*, in press, <https://doi.org/10.1016/j.cclet.2022.03.021>.



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