

Strategies and Challenges on Selectivity of Photocatalytic Oxidation of Organic Substances

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Most organic compounds are conventionally synthesized under high temperature and elevated pressure, resulting in significant energy consumption and wastage. Heterogeneous photocatalytic oxidation has the potential to provide a green route for the synthesis of the majority of industrially important chemicals. The major limiting factor affecting the efficiency of photocatalytic organic synthesis is the lack of high selectivity; therefore, substantial effort has been devoted to solving this problem. Responding to this fast-moving progress, this review gives an overview of the fundamental understanding of the reactive oxygen species involved in photocatalytic organic oxidations and furthermore, the general mechanisms of a few crucial oxidation reactions. The focus of this critical review is on the discussion of diverse strategies to improve the selectivity of high value chemicals, including band engineering, metal loading, hybrid materials, and defect engineering, with the primary aim of highlighting the catalyst design protocols based on the reaction mechanism. Finally, the difficulties and challenges of developing highly selective oxidation photocatalysts are comprehensively discussed in order to help direct the focus of future research.

industry has to upgrade traditional processes to “greener” synthesis routes.

Actually, an idea to address this issue has already been put forward by Giacomo Ciamician in *Science* in 1912: using photochemical processes to produce value-added organic chemicals.^[2] He predicted that abundant, renewable solar energy and mild reaction environment would replace harmful reagents and harsh conditions in organic synthesis. This idea was not brought to fruition until the discovery of the Honda–Fujishima effect in 1972.^[3] Titanium dioxide, in the form of thin film or nanoparticles, was found to simultaneously generate electrons and holes under light irradiation, thereafter taking part in a series of redox reactions. Since then heterogeneous photocatalysis by semiconducting materials has drawn tremendous attention and been extensively studied for water splitting,^[4] CO₂ reduction,^[5] environmental remediation,^[6] and organic

synthesis.^[7] In contrast to conventional thermal catalysis, both spontaneous reactions (Gibbs free energy difference $\Delta G_0 < 0$) and non-spontaneous reactions ($\Delta G_0 > 0$) can be initiated by photocatalysts. In spontaneous reactions, photocatalysts utilize light energy to overcome the activation barrier, facilitating reactions at an increased rate or under milder conditions. In non-spontaneous reactions, part of the light energy is transferred into the reaction products, storing as chemical energy.


The conception of photocatalysis was first widely applied to environmental purification, because a series of photocatalysts could easily decompose various kinds of organic pollutants into water and CO₂ (mineralization) with light irradiation under benign conditions. As for organic synthesis, despite the feasibility having been proved and great efforts having been made,^[8] most semiconductor-involved photocatalytic organic reactions are usually non-selective processes, especially in aqueous media.^[7] Improving selectivity in photocatalytic organic synthesis as a “greener” alternative to energy intensive and environmentally hazardous methods is therefore most sought after.

In recent years, more effort has been devoted to the study of photocatalytic organic synthesis. Consequently, there have been several reviews in regard to this field. In those pioneering accounts, Palmisano et al. summarized progress at the time in selective photocatalytic conversion and envisioned that these reactions would play a major role in the evolution of green chemistry.^[9] Some other reviews focused on titanium oxide-based materials and several interesting strategies for selective organic

1. Introduction

Since 1828, the year when urea was first synthesized from inorganic ammonium cyanate, organic synthesis has entered the historical arena, gradually forming an important cornerstone in human life.^[1] Upon nearly 200 years of investigation and practice, most organic chemicals are still synthesized under relatively harsh conditions, for example, high temperature and pressure, also generating a large amount of hazardous by-products. In the 1990s, with a consensus on the consequences of chemical pollution and increasing resource demand, “green chemistry” was proposed, so that if we cannot eliminate the use or generation of hazardous substances, we can minimize them. Along with more stringent environmental policies, the chemical

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transformation were introduced.^[7,10] Later, researchers' attention has shifted from large-bandgap, UV-activated photocatalysts to visible-light-induced ones. Such trends were pointed out in a review on inorganic semiconductors responsive to visible light.^[11] The polymeric materials, and some plasmonic photocatalysts for organic synthesis were later summarized.^[12] In parallel, another review focused on the selective transformation of biomass-derived substrates, a newly developed alternative for the production of value-added chemicals and fuels.^[13] Deeper understandings in this field have been acquired over time. Comparison between photocatalytic organic degradation and organic synthesis revealed that unlike photocatalysts for organic degradation, photocatalysts for organic synthesis should be highly customized on a case-by-case basis.^[14] Another review linked the performance of different catalysts to the photo-induced active species and offered several strategies to improve conversion rate and selectivity.^[15] Other published reviews on this topic have been more specific, such as focusing on semiconductor-based core-shell nanocomposites.^[16] More recently, various CdS-based photocatalysts have been discussed,^[17] and low dimensional (1D and 2D) photocatalysts have been presented in other interesting reviews.^[18]

Behind polymerization, selective oxidation is the second largest industrial process, contributing ≈30% of total production in the modern chemical industry.^[19] Selective oxidation reactions thus play a vital role in organic synthesis and have drawn particular attention. Numerous compounds and intermediates like alcohols, epoxides, aldehydes, ketones and organic acids, can be prepared by selective oxidation catalysts. Given the recent surge of catalysts' discovery and understandings on selective photocatalytic oxidation, a critical review is crucial for the next step development, taking into account that the major reviews in this area are 3 to 5 years old. Herein, the basic mechanism of photocatalytic organic oxidation and an overview of reactive oxygen species (ROS) that are commonly produced in-situ in a photocatalytic system are first briefed. The general mechanisms of several key oxidation reactions are then described, forming the basis to approach the major topic of this critical review and to manipulate selectivity that is a well-known paramount in organic synthesis. More importantly, six strategies to improve selectivity have been detailed and discussed, namely band engineering, metal loading, hybrid materials, defect engineering, morphology and crystallization control, and surface states manipulation, with the aim of elucidating the design protocols to direct the subsequent photocatalyst's development for highly selective organic synthesis. Finally, a rather detailed description of challenges and possible future work is proposed, which would be informative for researchers in this and the related areas.

2. Mechanisms

2.1. Heterogeneous Oxidation by Semiconductor Photocatalysis

Typically, semiconductor-involved photocatalysis is a process where semiconductors are activated by light, generating energetic electrons and holes to initiate oxidation and reduction reactions. In other words, incident light with energy higher than the semiconducting photocatalyst's bandgap could generate electrons and holes simultaneously, where the electrons can be

excited to the conduction band (CB), leaving photoactivated holes in the valence band (VB). Generated electrons and holes could recombine, or migrate to the surface of the catalyst, then initiating a variety of photoredox reactions. Because photocatalysis is practically conducted in the presence of water under aerobic conditions, involving oxygen and/or water as reaction species, a series of ROS, including superoxide radical ($\cdot\text{O}_2^-$), hydrogen peroxide (H_2O_2), hydroxyl radical ($\cdot\text{OH}$) and singlet oxygen ($^1\text{O}_2$), could be generated from surrounding oxygen molecules, water, or OH groups attached on the catalyst's surface. Together with the photogenerated holes, these oxygen species are the key compounds to initiate photocatalytic organic oxidations.

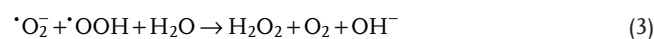
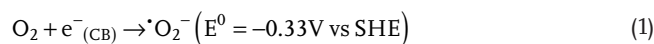
In the well-documented photocatalytic degradation, photoactivated holes and free radical species (especially $\cdot\text{OH}$) are considered to be the main oxidants; they can mineralize organic compounds into CO_2 and water unselectively. Similarly, in organic synthesis processes, these strong oxidants are inevitably formed in aqueous media, facilitating nonselective oxidation, and thus reducing the selectivity to the target product. Therefore, careful control of the formation of ROS is vital in selective photocatalytic organic synthesis and the formation processes of these ROS are first presented below.

2.2. Reactive Oxygen Species

Reactive Oxygen Species (ROS) are generated via the interaction of photoactivated charge carriers with the surrounding medium; the type of photocatalyst or solvent used, therefore playing an important role in a photocatalytic system. Understanding the formation and properties of ROS provides clues to improve catalytic activity and selectivity as these species are the primary oxidants besides photogenerated holes in photooxidation reactions (Figure 1).^[20]

2.2.1. Superoxide Radical ($\cdot\text{O}_2^-$)

Semiconductors with a CB edge more negative than the potential of $\text{O}_2/\cdot\text{O}_2^-$ (sometimes denote O_2^-) could transfer photoactivated electrons to the π^* orbitals of oxygen molecules, generating superoxide radicals (reaction 1). As a moderate oxidant, $\cdot\text{O}_2^-$ could either participant in or directly initiate selective oxidation of organic compounds. Moreover, relatively long survival time enables $\cdot\text{O}_2^-$ to migrate long distances in the reaction media, thus allowing the oxidation reaction taking place beyond the surface of the catalyst.^[21] Nevertheless, excessive accumulation of $\cdot\text{O}_2^-$ could overoxidize organic molecules and finally result in mineralization.^[22] In acidic media (pH < 4.8), $\cdot\text{O}_2^-$ could be easily protonated to hydroperoxyl radical ($\cdot\text{HO}_2$) (reaction 2) and further disproportionated to H_2O_2 (reaction 3).



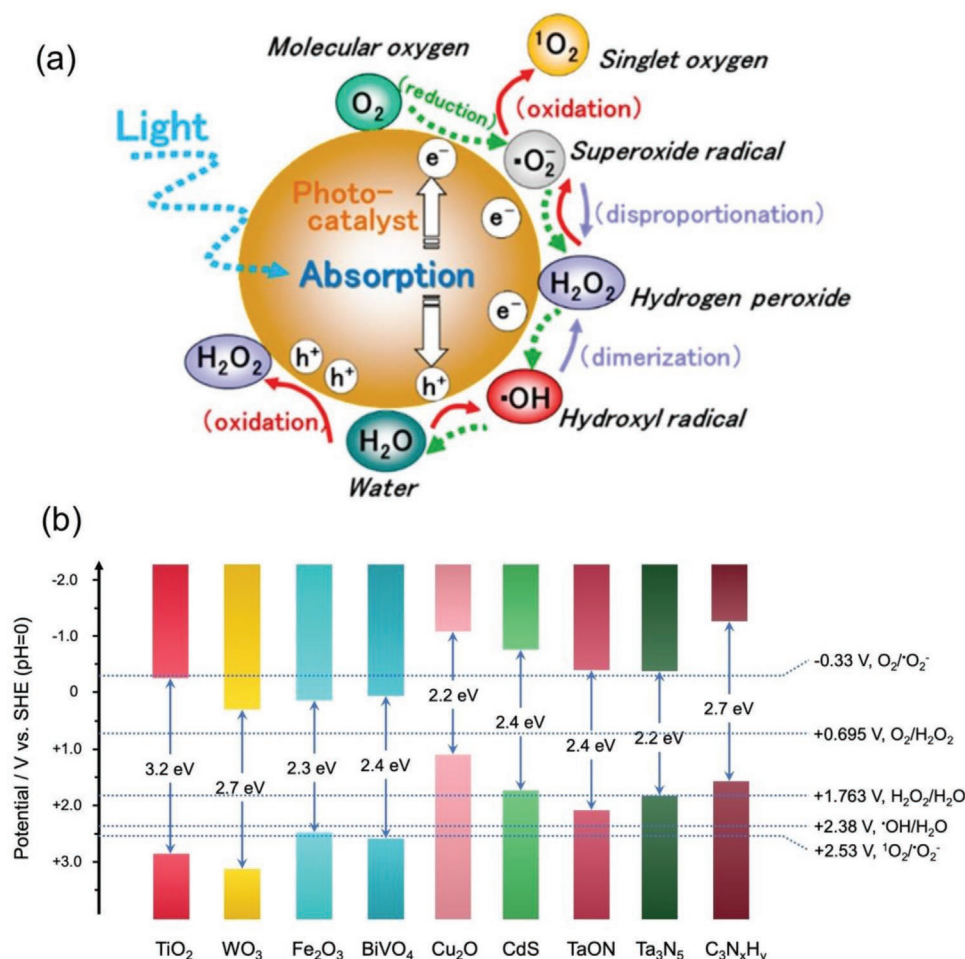
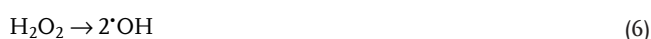
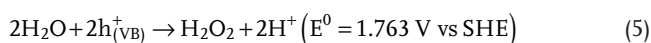
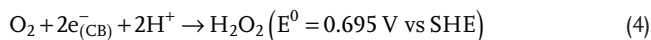


Figure 1. a) Reactive oxygen species generated in the photocatalytic reduction of oxygen and oxidation of water. Reproduced with permission.^[20] Copyright 2017, American Chemical Society. b) Redox potentials of reactive oxygen species and band edge positions of typical semiconductors for organic oxidation.

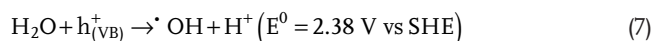
2.2.2. Hydrogen Peroxide

If the CB of the semiconductor is not sufficient to reduce O_2 by a single-electron process, the two-electron reduction is the only way to activate O_2 by forming hydrogen peroxide (H_2O_2) (reaction 4). In aqueous media, H_2O_2 could also be generated by two-hole oxidation from H_2O (reaction 5). As a stronger oxidant than oxygen, H_2O_2 can directly oxidize organic chemicals. Moreover, H_2O_2 could decompose into hydroxyl radicals ($\cdot OH$) (reaction 6), which can activate strong bonds like unsaturated sp^2 C–H bonds of benzene, followed by the complete mineralization.^[23] Thus the decomposition of H_2O_2 is considered a key step in environmental remediation, whether H_2O_2 is added or in situ generated. This also generates another challenge to manipulate the selectivity of the expected organic production.



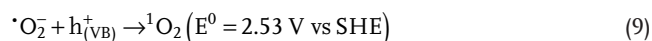
2.2.3. Hydroxyl Radicals

With sufficient energy, photogenerated holes could oxidize adsorbed water or surface-attached hydroxyls into hydroxyl radicals ($\cdot OH$) (reaction 7). Though the mechanistic implications are still unclear, $\cdot OH$ radicals are widely regarded as the strongest oxidative species in organic oxidation and thus extensively applied in photocatalytic remediation of organic pollutants. Nevertheless, in selective organic oxidation, $\cdot OH$ can result in the nonselective oxidation of organics into CO_2 and water instead of value-added organic chemicals, therefore great efforts have been made to suppress the formation of $\cdot OH$ in order to improve selectivity of the reaction.^[24] It should be noted that, because of a higher diffusion coefficient ($3.0 \pm 0.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) compared with H_2O_2 ($1.1 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) or $\cdot O_2^-$ ($2.9 \pm 0.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$),^[25] $\cdot OH$ has a particular influence on the oxidation of organic molecules that have a weak affinity to the catalyst surface.



2.2.4. Singlet Oxygen

Singlet oxygen ($^1\text{O}_2$) could be generated by transforming energy from the triplet state of a photosensitizer to a ground state oxygen molecule (reaction 8). It has been suggested that the oxidation of $\cdot\text{O}_2^-$ by photoactivated holes could also yield $^1\text{O}_2$ species (reaction 9).^[26] As a moderate oxidant compared with $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, $^1\text{O}_2$ can effectively oxidize organic chemicals while avoiding the overoxidation.



2.3. Selective Photocatalytic Oxidation

With the rapid development of materials science, there have been tremendous application and demand of catalytic organic synthesis. Photocatalysis has been applied in the oxidation of various organic chemicals, typically including alcohols, hydrocarbons, aromatics, and amines, which shows distinctive aspects from the conventional approaches, for example, very moderate condition and very benign to the environment. Fundamental understandings on the mechanisms behind these reactions are critical to improve catalyst activity and selectivity, and avoid complete mineralization of organic substance to CO_2 and water. The following sections will mention these attractive reactions one by one, and the effect of reaction environment, which will help understand the strategies discussed later for selectivity control that is paramount in organic synthesis.

2.3.1. Oxidation of Alcohols

The selective oxidation of alcohols is a major route to synthesis carbonyl chemicals. Conventional oxidation of alcohol often involves thermal-catalytic processes or strong oxidizing agents such as chromate, permanganate, and hypervalent iodine.^[27] These processes inevitably generate hazardous wastes and inherently suffer from low selectivity toward target high value chemicals due to the harsh conditions used. In contrast, photocatalytic oxidation of alcohol provides a more environmental-friendly alternative for carbonyl compounds synthesis. We next discuss the basic mechanism of alcohol oxidation taking benzyl alcohol oxidation as a model reaction.

A mechanism was proposed based on the direct participation of photoactivated holes and $\cdot\text{O}_2^-$.^[22] Benefited from the sufficiently negative CB of mesoporous carbon nitride (CN) polymer, $\cdot\text{O}_2^-$ could be generated by the reduction of molecular oxygen under visible light. Benzyl alcohol was first reacted with photogenerated holes to deprotonate on the basic surface of CN to form corresponding radical. The recombination of this radical and $\cdot\text{O}_2^-$ finally formed the ketone molecule. One might see that there were different opinions about the role of $\cdot\text{O}_2^-$ in benzyl alcohol oxidation. When using $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ nanobelts as a photocatalyst, only the photoactivated holes took part in the oxidation of benzyl alcohol. The oxidizing capability of the holes, that is, the VB position of the photocatalyst, largely affected the

selectivity.^[28] Though the activation of oxygen molecules into $\cdot\text{O}_2^-$ was important, this process was most regarded to be inhibiting the recombination of photogenerated charge carriers.

On the other hand, the subsequent studies supported the radical $\cdot\text{O}_2^-$ recombination mechanism and brought some different insights.^[29] It was reported based on a plasmonic catalyst of Au supported on BiOCl containing oxygen vacancies. Upon the excitation of Au nanoparticles, hot electrons were trapped at oxygen vacancies, while hot holes remained on the Au surface (Figure 2). Although the hot electrons and holes were spatially separated, the unique structure of the surface of BiOCl allowed the co-adsorption of O_2 and benzyl alcohol, ensuring the hot electrons and holes worked cooperatively in benzyl alcohol oxidation. Hot holes on Au nanoparticles efficiently attracted the $\alpha\text{-H}$ of benzyl alcohol to form carbon-centered radicals, while hot electrons could easily transfer to adsorbed O_2 , generating $\cdot\text{O}_2^-$ species. Closely located carbon-centered radicals and $\cdot\text{O}_2^-$ species were prone to combine toward the formation of an oxygen-bridged structure. Concerted bond cleavage of this structure would form benzaldehyde. More recently, it was found that In_2S_3 nanosheets with abundant S vacancies could effectively oxidize benzyl alcohol.^[30] Although the holes participated in the reaction, experimental results showed that the excellent oxidation ability of In_2S_3 was due to the facilitated $\cdot\text{O}_2^-$ generation. This study implied that radical $\cdot\text{O}_2^-$ recombination could be the main mechanism in photocatalytic alcohol oxidation.

Although the decisive evidence for the actual mechanism of alcohol oxidation has yet elucidated, especially the role of $\cdot\text{O}_2^-$ as debatable, all current results indicate that the primary oxidants should be photoactivated holes and $\cdot\text{O}_2^-$. Therefore, for a semiconducting photocatalyst, VB position, the electron affinity of the substrate, and the ability to generate $\cdot\text{O}_2^-$ are all of great significance when applied for selective alcohols oxidation.

2.3.2. Oxidation of Saturated C–H Bonds

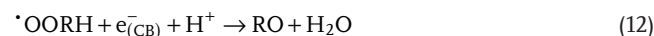
Compared with selective alcohol oxidation, the selective oxidation of saturated C–H bonds is more difficult due to the higher bond energy. In this field, most researchers have focused on two reactions: toluene to benzaldehyde and cyclohexane to cyclohexanone. Combining most of the literature information,^[31] the mechanism of hydrocarbons photooxidation can be summarized by the following reactions. Generally, the hydrocarbon is first oxidized to alkyl radicals ($\cdot\text{RH}$) via photogenerated holes:



This process is widely recognized as a rate-determining step due to the inertness of saturated sp^3 C–H bonds. Molecular O_2 can react with $\cdot\text{RH}$ with a diffusion-controlled rate to generate peroxy radicals ($\cdot\text{OORH}$):



Subsequently, resulting $\cdot\text{OORH}$ can react with various ROS to generate alcohols and carbonyl compounds:



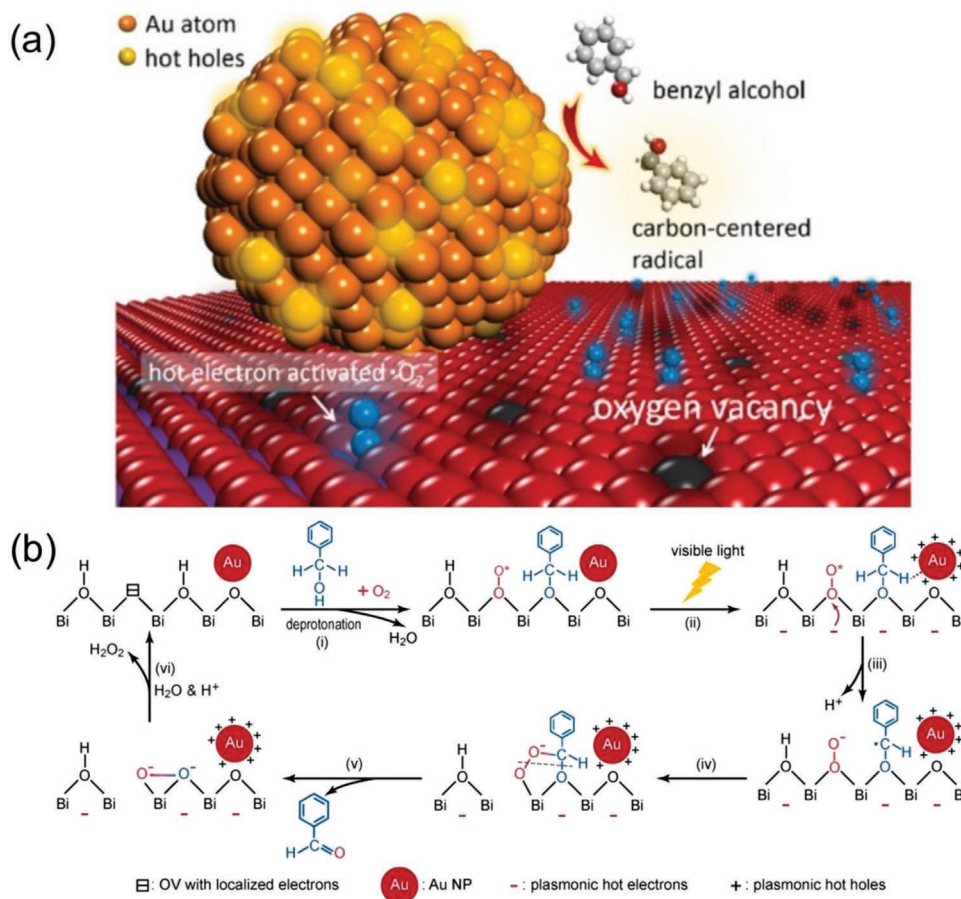
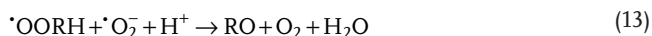
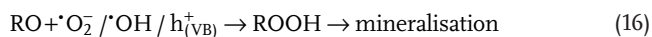


Figure 2. a) Schematic illustration of the generation of reactive species over Au loaded BiOCl with oxygen vacancies. b) Proposed mechanism of selective benzyl alcohol oxidation. Adapted with permission.^[29] Copyright 2017, American Chemical Society.



If the reaction media contains excess strong oxidants like $\cdot OH$, further oxidation of target products will take place, even up to complete mineralization:



Therefore, adsorption–desorption equilibria of reactants and reaction intermediates are two important factors determining the final product distribution.

2.3.3. Oxidation of Benzene

Phenol is an important organic chemical which can be used in a wide range of applications. Conventionally it can be produced by sulfonation, chlorination or cumene processes.^[32] All

these synthesis methods require harsh conditions and involve hazardous chemicals. Direct hydroxylation of benzene provides a green alternative route and makes it possible to improve selectivity as benign conditions are used in the process. The direct hydroxylation of benzene means to activate the unsaturated sp^2 C–H bonds, this is similar to the activation of the saturated form: initiated by photoactivated holes with sufficient oxidizing ability. The oxidation potential of benzene in acetonitrile was reported to be 2.48 ± 0.03 V (versus SCE),^[33] thus a photocatalyst with sufficiently positive VB is necessary for this reaction. Subsequently, the formed cationic radical species of benzene are further attacked by various ROS (mainly O_2 or $\cdot O_2^-$), finally transformed into phenol molecules (Figure 3).^[34] In the presence of excessive strong oxidant species, phenol could be overoxidized into a variety of phenol derivatives including hydroquinone, benzoquinone, finally CO_2 and H_2O .^[35]

Oxidization via photogenerated holes requires benzene to contact the catalyst surface. For those photocatalysts with poor adsorption ability of benzene, holes react primarily with H_2O molecules, yielding $\cdot OH$ that subsequently attack the benzene ring to produce hydroxycyclohexadienyl radical.^[36] The release of the proton radicals from the hydroxycyclohexadienyl radical would result in the formation of phenol.

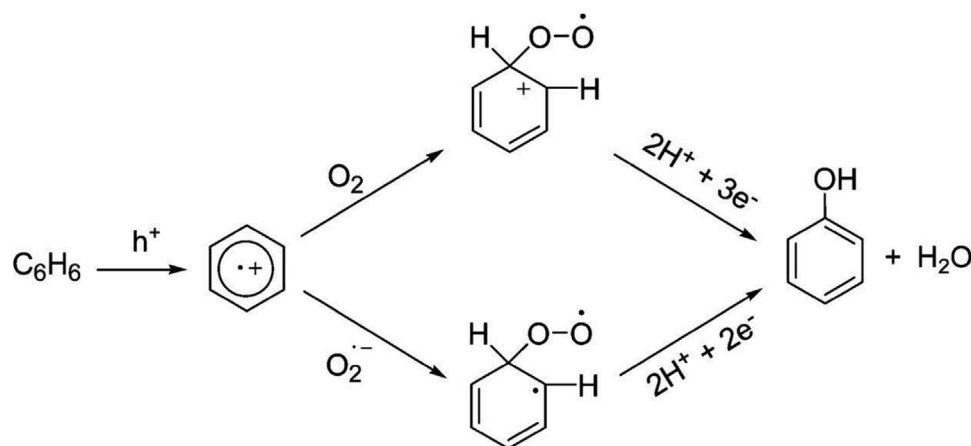


Figure 3. Proposed mechanism for the production of phenol from benzene through a hole transfer process using O_2 as the oxygen source. Reproduced with permission.^[34] Copyright 2010, American Chemical Society.

2.3.4. Oxidation of Amines

Imines, a group of chemical compounds containing $C=N$ bonds, are important building blocks for the production of pharmaceuticals, pesticides, and other value-added chemicals. Currently, they could be prepared by the dehydration of amines and carbonyl compounds such as aldehydes, in which dehydrating agents and Lewis acid catalysts are involved, therefore generating excessive wastewater. In 2011, TiO_2 -mediated aerobic oxidation of amines for imines formation was realized under UV light.^[8d] Since then, considerable efforts have been devoted to photocatalytic production of imines. The general mechanism in amines oxidation begins with the generation of hole-electron pairs (Figure 4). The holes initiate the deprotonation of amine to form a neutral carbon-centered radical. At the same time, the electrons activate molecular oxygen into $\cdot O_2^-$. Then, the two radicals react with each other to generate H_2O_2 and NH -imine intermediates which are further transformed into the desired imines.^[37]

So far, the possible mechanisms in the selective photocatalytic oxidation reactions have been briefed, mainly involving the roles of oxidant species. It should be noted that all mechanisms reported in the literature are very general. The actual reaction routes and final products differ from different photocatalysts, affected by band positions, charge carrier transfer, and the

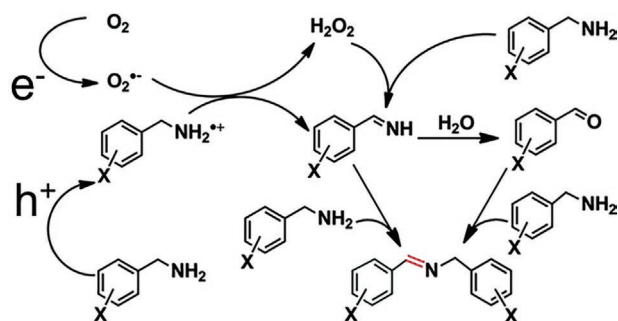


Figure 4. Proposed mechanism for benzylamine aerobic oxidation reaction pathways over layer double hydroxide. Adapted with permission.^[37] Copyright 2014, The Royal Society of Chemistry.

affinity of the photocatalysts to reactants. On the other hand, new photocatalytic reaction routes are emerging quickly in recent years, for example, the epoxidation of alkenes.^[38] Predictably this will intensify the related research area and bring to the forefront of green chemistry.

2.3.5. Reaction Environment

Despite the intrinsic characteristics of photocatalysts, the reaction environment also plays an important role. For example, the employed solvent can strongly affect the interaction between the photocatalyst surface and the substrate. When using TiO_2 to oxidize cyclohexane in various solvents, selectivity of cyclohexanol and cyclohexanone were found to be dependent on adsorption.^[39] Selectivity was higher in polar solvents because cyclohexanol adsorbed on TiO_2 to a lesser extent. In non-polar solvents, cyclohexanol preferentially adsorbed onto TiO_2 thus being completely mineralized.

When water is used as the solvent in photocatalytic oxidation reactions, it could be easily adsorbed on the photocatalyst surface and then oxidized by photoactivated holes, generating highly oxidizing $\cdot OH$. Thus, an organic solvent such as acetonitrile is often used in photocatalytic oxidation reactions. Organic solvents differ in viscosity, polarity, polarizability, and hence they have different abilities to stabilize intermediate species. Solvent choice can therefore provide another method for controlling selectivity.^[40]

One of the aims of photocatalytic oxidation is to avoid harsh operating conditions such as high temperature and pressure, which are typically required in conventional industrial routes. Therefore the majority of photocatalytic oxidation reactions are conducted at room temperature. However, earlier research did investigate the effect of reaction temperature. In the oxidation of liquid cyclohexane using acetonitrile as a solvent, it has been found that the activity was higher in the medium temperature region (295–328 K).^[41] At low temperature (<295 K), the limiting step became the desorption of the main product while at temperature > 328 K, the limiting step became the adsorption of the reactant.

When establishing a heterogeneous photocatalytic process for organic synthesis by oxidation, the major challenge is the generation of moderate oxidizing species, which can avoid the loss of products due to complete mineralization. Obviously, controlling the formation of ROS is a challenging yet rewarding task. In the next section, we will discuss various strategies to minimize the mineralization and shift the reaction toward the desired products thus achieving excellent selectivity.

3. Improving the Selectivity of Photocatalytic Oxidation

The most important for organic synthesis is to control the selectivity to products, which is also the key challenge for photocatalysis due to the extremely strong oxidative capability of diverse ROS. The following focuses on the proved strategies to overcome the challenge.

3.1. Band Engineering

One issue with a semiconductor for photocatalysis for selective organic synthesis is the highly oxidative environment due to the deep VB of the semiconductor that can completely mineralize the organic substances. As indicated above, the oxidation of an organic substrate can be initiated either directly by holes, or through an indirect route, in which ROS are generated and then in turn oxidize the organic molecules. Therefore, manipulating the band structure, especially the band positions of a given photocatalyst is an effective strategy to minimize the over-oxidation of organic substrates in photocatalytic oxidation reactions, thereby tuning selectivity.

Different semiconductors may have significantly different CB and VB potentials, which determine the thermodynamic feasibility of what reactions could proceed, and the potential products. Therefore, while evaluating the thermodynamic driving forces for the reactions of interest, enhanced selectivity could be achieved by the appropriate selection of a semiconductor. An example is the selective photocatalytic oxidation of benzene to phenol in water containing molecular oxygen. Pt nanoparticles loaded WO_3 was reported to photocatalytically generate phenol from benzene with high selectivity (e.g., 74% at 69% of benzene conversion), which was much higher than that over TiO_2 , which produced CO_2 as the main product.^[36a] The difference in selectivity was attributed to the distinction of CB positions between WO_3 and TiO_2 . Photogenerated electrons on Pt/WO_3 tended to initiate two-electron reduction of O_2 , generating H_2O_2 , which could not over-oxidize produced phenol. In contrast, the electrons at the CB of TiO_2 readily generated oxygen radical species such as $\cdot\text{O}_2^-$, which led to the successive oxidation of phenol to CO_2 , thus reducing the selectivity.

TiO_2 could generate various highly oxidative radical species under UV light, which generally leads to a high degree of mineralization. Optimizing solvents to control the lifetime and speciation of radicals could enhance selectivity to some extent. However, cases where a high selectivity was achieved are relatively scarce.^[42] Altering the electronic properties of TiO_2 to shift the reaction selectivity has been proved to be a feasible

way. Through doping Ru into TiO_2 nanotubes, the selectivity of toluene oxidation to benzaldehyde under UV irradiation was largely enhanced.^[43] The energy levels of introduced Ru ($\text{Ru}^{3+/4+}$ states) were located at a more positive position than the CB of TiO_2 , with an insufficient potential for single-electron reduction of molecular oxygen. Since the Ru levels tended to trap the photoactivated electrons, the generation of excessive $\cdot\text{O}_2^-$ was significantly suppressed, thus inhibiting the overoxidation of benzaldehyde to benzoic acid. This strategy was also adopted to alter VB positions, as some experiments indicated that the selectivity of photocatalytic oxidation could also highly depend on the VB position of semiconductors.^[28] For example, when the N- and S-doped TiO_2 photocatalysts were under 442 nm light irradiation, a greater amount of $\cdot\text{O}_2^-$ was generated than that from the pristine TiO_2 (P25) irradiated at 325 nm.^[24b] Moreover, S-doped TiO_2 mainly produced $\cdot\text{O}_2^-$, while N-doped TiO_2 generated more H_2O_2 under the same condition. This difference was attributed to the multivalence property of sulfur atoms which may promote the decomposition of H_2O_2 . In another example, by modifying TiNb_2O_7 with nitrogen dopants, new N 2p orbitals were formed.^[44] Combining with the introduction of oxygen vacancy levels, the electronic structure of TiNb_2O_7 was modulated to a narrower band gap for more photoabsorption. When the modified photocatalyst was used in the conversion of benzylamine under green light irradiation, the yield and selectivity of N-benzylidenebenzylamine were significantly improved compared to unmodified samples.

In recent years, the rapid development of metal-organic frameworks (MOFs) has brought new impetus for the study of selective oxidation reactions. MOFs are constructed from metal or metal cluster nodes interconnected with multi-dentate organic linkers, in which the metal nodes serve as semiconductor quantum dots while the organic linkers serve as the antenna to sensitize these quantum dots. In 2008, isoreticular MOFs with a series of organic linkers were demonstrated to oxidize gas-phase propylene under UV irradiation.^[45] Results showed that the band gap of these MOFs could be altered by changing the organic linker. Moreover, the change in bandgap resulted in different activity and product distribution. Later, the discovery of Ti-containing MIL-125(Ti) represented another breakthrough in photocatalytic oxidation, though it could only be activated by UV light.^[46] To expand the light absorption of MIL-125(Ti) to the visible region, the organic linker BDC was substituted on the aromatic ring with amine groups.^[47] Experimental results showed that only a small amount of $-\text{NH}_2$ motif is sufficient to reduce the bandgap of the monoaminated series of MIL-125(Ti) analogues. This strategy was successfully applied in the aerobic oxidation of amines under visible light.^[48] A wide range of amines could be oxidized into imines with yields ranging from 45% to 93% over NH_2 -MIL-125(Ti).

Except for substituting organic linkers, the light absorption property of MOFs could also be tuned by doping ions into metal clusters. For example, after incorporating Fe^{3+} ions into a representative MOF, Uio-66, metal-to-cluster charge transfer could be induced, which reduced the bandgap and resulted in the extended visible light response.^[49] By sharp contrast to the completely inert Uio-66, the unique electron transfer enabled Fe-Uio-66 to oxidize H_2O into $\cdot\text{OH}$ and thereafter oxidize hydrocarbons, particularly toluene, under visible light irradiation.

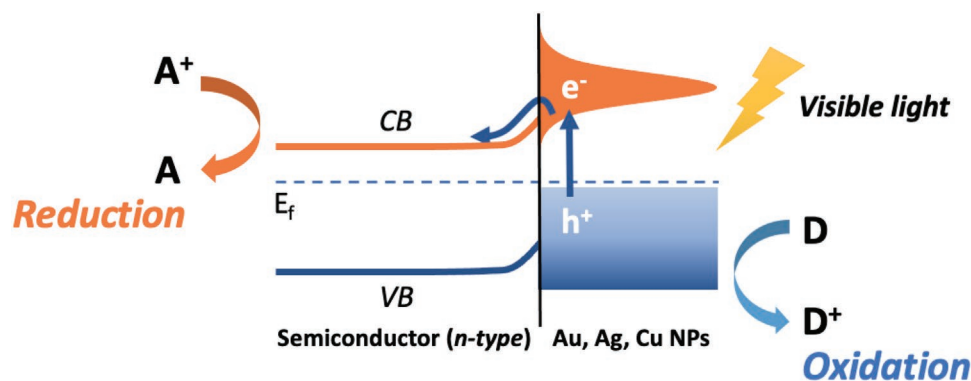


Figure 5. Surface plasmonic metal (Au, Ag, or Cu) NPs for visible light induced reactions.

3.2. Metal Loading

In the pioneering studies on photocatalytic oxidation, titanium dioxide was often used as a photocatalyst as at that time researchers already had some understanding on its role in the decomposition of harmful organic compounds. However, the application of pristine TiO_2 in organic synthesis was unsuccessful because reactions usually lack satisfied selectivity. With its deep VB, TiO_2 normally creates a highly oxidizing environment that leads to complete mineralization, therefore generating unexpected products. Moreover, its large bandgap confines its photoabsorption in the UV region. Therefore, metal loading, as an effective strategy to tackle this problem, has been extensively applied in relevant studies.

With regard to the interfacial charge transfer, there are two mechanisms proposed when loading metals on the surface of photocatalysts: the plasmonic effect and the Schottky junction. For plasmonic metals like Au, Ag, and Cu, when the frequency of incident photons is close to the natural frequency of surface electrons oscillation against the restoring force of positive nuclei, the collective oscillation of electrons will take place, which is called surface plasmon resonance (SPR) (Figure 5). Due to the SPR effect, the absorbance spectra of surface plasmon bands generated by Au (25 nm diameter), Ag (38 nm diameter), and Cu (133 nm diameter) spherical nanoparticles show strong visible-light absorption. Such absorption maxima, for example, at 530, 400, and 580 nm, vary with the particle size, respectively,^[50] thus providing a feasible way to tune the redox potential of the active electrons and holes by manipulating the nanoparticles' size. When loading plasmonic nanoparticles on semiconducting photocatalysts like TiO_2 , visible light could excite electrons below the Fermi level (E_f) of the plasmonic nanoparticles to the surface plasmon (SP) states, leaving positive charges (h^+) below E_f . Electrons at SP states subsequently transfer into the CB of semiconductors, and ultimately to electron acceptors like O_2 , facilitating efficient selective aerobic oxidation. In the meantime, h^+ left in nanoparticles could react with the organic substrate to complete the photocatalytic cycle,^[12] these holes have a much weaker oxidation potential than those in the VB of TiO_2 . The other major mechanism involved here is the Schottky junction, a potential energy barrier formed at a metal–semiconductor interface, which stops the electrons transferring back to the nanopar-

ticles across the Schottky junction—this is the reason why Schottky junction enhances charge separation.

Taking Au loaded CeO_2 as an example, it was used for the selective oxidation of benzyl alcohols to corresponding benzaldehydes in aqueous suspension under visible light.^[51] Electrons in Au nanoparticles were excited and injected into the CB of CeO_2 , and the electron depleted Au nanoparticles oxidized organic compounds. The role of hot electrons was further presented in Au loaded $BiOCl$.^[29] Under visible light irradiation, plasmonic hot electrons were trapped and transferred to adsorbed O_2 , producing $\cdot O_2^-$ radicals. Meanwhile, the loss of electrons lowered the Fermi level of Au nanoparticles, endowing with the oxidation ability.^[52] Therefore, benzyl alcohol was mildly oxidized on the Au surface to corresponding carbon-centered radicals and then combined with $\cdot O_2^-$ radicals to form benzaldehyde. When using Au nanoparticles loaded TiO_2 , amines were efficiently oxidized to imines without overoxidation, showing the mild oxidation ability of Au nanoparticles.^[53] All above results suggested that Au nanoparticles could effectively generate electrons and mild oxidative holes under visible light irradiation, both species are beneficial to the selective oxidation.

Au loaded semiconductors could also be employed in oxidation reactions requiring relatively strong oxidants, for example, benzene to phenol reaction. The oxidation potential of benzene in acetonitrile was reported to be about 2.48 V (versus SCE),^[33] thus a photocatalyst with sufficiently positive VB is required for this reaction. Holes in Au nanoparticles have a significantly lower oxidation potential; obviously, the Au nanoparticles could not directly take part in the benzene oxidation. However, Au loaded $Ti_{0.98}V_{0.02}O_2$ was found to oxidize benzene under UV light.^[54] Although there was no significant phenol production under visible light on Au loaded $Ti_{0.98}V_{0.02}O_2$, loading Au on the catalyst indeed boosted the production of phenol under UV light. Combined with other results, they argued that the role of Au nanoparticles was mainly for charge separation. Au nanoparticles selectively stored photoexcited electrons and in turn maximized holes utilization on $Ti_{0.98}V_{0.02}O_2$. The reason why electrons transferred from $Ti_{0.98}V_{0.02}O_2$ to Au nanoparticles rather than the opposite was that only UV light could not trigger a significant SPR effect in Au nanoparticles due to the mismatch of the absorption maximum of Au nanoparticles with the UV wavelength, causing the electron flow to the Fermi level of Au nanoparticles.^[55]

Apart from gold, other noble metals, such as Pt and Pd, were also widely used as cocatalysts in selective photocatalytic oxidation. For example, Pt nanoparticles supported on anatase TiO₂ was reported to promote selective alcohol oxidation under visible light irradiation ($\lambda > 450$ nm) at room temperature.^[55] Visible light excited electrons in Pt nanoparticles, the electrons then transferred to the anatase CB. The positively charged Pt particles mildly oxidized substrates, whereas the electrons in TiO₂ were consumed by the reduction of O₂—similar to the Au loaded photocatalysts. Further experiments indicated that the activity of this photocatalyst depended on the height of the Schottky barrier and the number of perimeter Pt atoms at the Pt/TiO₂ heterojunction, which were affected by the amount and size of Pt nanoparticles. As reported, increasing the amount of metal loaded onto the semiconductor led to a larger Schottky barrier due to the decrease in the Fermi level of the semiconductor,^[56] which is arguable. Increased Schottky barrier would suppress electron transfer from photoactivated Pt nanoparticles to TiO₂. On the other hand, the electrons of Pt nanoparticles mainly transferred to TiO₂ via the peripheral Pt atoms; hence, the number of perimeter Pt atoms may affect the transfer efficiency. Therefore, subtly tuning the amount and size of Pt nanoparticles was of great significance in this reaction. Specifically, the catalyst with 2 wt% Pt, containing 3–4 nm Pt nanoparticles showed the highest photocatalytic activity. Later, the same group found Pd loaded TiO₂ in alcohol containing primary amine could efficiently promote N-monoalkylation of amine with alcohol, producing the corresponding secondary amine with almost unity yield under $\lambda > 300$ nm light.^[57] In this reaction, Pd first oxidized alcohol on the photoactivated TiO₂, then condensation of the formed aldehyde with amine occurred on the TiO₂ surface. Finally, the formed imine was hydrogenated by the surface H atoms on the Pd particles. Calculating the number of surface Pd atoms revealed that the Pd atoms on the triangle site of Pd nanoparticles were the active site for hydrogenation. Meanwhile, larger triangle sites strongly adsorbed alcohol and suppressed imine hydrogenation. Because the rate-determining step was the imine hydrogenation, the photocatalysis selectivity was closely related to the size of the Pd nanoparticles. As a result, the catalyst containing 0.3 wt% Pd and 2–2.5 nm Pd particles showed the highest activity for imine hydrogenation. The above results highlight the importance of the size and amount of metal nanoparticles; both parameters have significant influences on the plasmonic effect and Schottky junction, then affecting charge transfer and oxidation capacity of catalysts while the interpretation is arguable, requiring further investigation.

Considering the high cost of noble metals, researchers have been increasingly interested in non-noble metals loaded catalysts. For instance, Ni clusters were presented having the ability to boost photocatalytic synthesis of imines from amines oxidation via the release of hydrogen (H₂).^[58] By constructing in situ photodeposited Ni clusters on the CdS photocatalyst, imines were formed at a dramatically improved rate under visible light illumination. Mechanistic investigation revealed that the desorption of photogenerated hydrogen atoms during the dehydrogenation of amines was significantly promoted on Ni clusters, thus resulting in the fast formation of C-centered radicals and then the generation of imines.

In some cases, loading monometal on photocatalysts cannot completely solve the problem. For example, TiO₂ in O₂-saturated water can generate H₂O₂ via the two-electron reduction of O₂ under UV light, provided the presence of electron donor such as alcohols. The problem is that the yield of H₂O₂ is significantly low (<0.2 mM).^[59] This is because the generated H₂O₂ can react with OH groups on the TiO₂ surface and is converted to peroxy species (Ti–OOH), then decomposed by the reduction of electrons. Loading Au nanoparticles can collect and trap electrons from the TiO₂ CB owing to the effect of the Schottky junction. This suppresses the reduction of Ti–OOH species. Moreover, the two-electron reduction of O₂ is favored on the Au nanoparticles; therefore, the introduction of Au can boost the efficiency of H₂O₂ production. However, H₂O₂ molecules tend to strongly adsorb onto the Au nanoparticles and be decomposed into $\cdot\text{OH}$ and OH⁻ by the reduction of electrons.^[60] In this context, TiO₂ loaded with Au–Ag bimetallic alloy particles was demonstrated to efficiently produce H₂O₂ from an O₂-saturated ethanol/water mixture under UV irradiation.^[59] The introduction of Ag atoms could suppress photocatalytic decomposition of formed H₂O₂ due to the decreased adsorption of H₂O₂ onto the Au atoms. Another example is Au–Pd/ZnIn₂S₄ composite, which could selectively oxidize aromatic alcohol under visible light.^[61] The reason for the introduction of Pd was because Pd nanoparticles possessed superior adsorption and activation ability for O₂. Hot electron excited in Au would inject into Pd nanoparticles to generate $\cdot\text{O}_2^-$. In another case, visible-light irradiation ($\lambda > 450$ nm) of Au–Cu alloy particles supported on TiO₂ was reported to successfully promote aerobic oxidation without catalyst deactivation.^[62] Compared with Au loaded TiO₂, the Au–Cu alloy loaded catalysts exhibited much higher activity owing to the alloying effect. In the meantime, the collective oscillation of electrons in the surface Au atoms could reduce the oxidized Cu atoms and keep the Au–Cu alloying effect (Figure 6). Bimetal loading gives photocatalysts novel properties and new possibilities, further studies in this strategy could lead to the discovery of high-performance photocatalysts, which effectively promote the production, separation, and utilization of photoexcited carriers in organic synthesis.

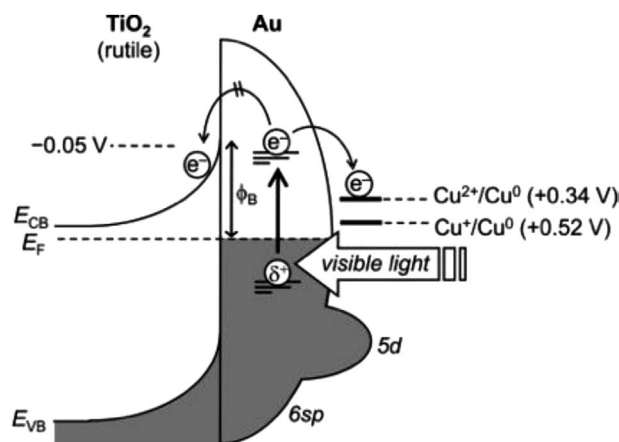


Figure 6. Possible energy diagram (versus NHE) for plasmon-activated AuCu/P25 catalysts under visible-light irradiation. Reproduced with permission.^[62] Copyright 2013, John Wiley & Sons.

Since the first terminology proposed by Zhang et al. in 2011,^[63] single atomic-site catalysts (SACs), involving the isolated metal atoms stabilized on appropriate supports, have become one of the most innovative and active research frontiers in the entire field of heterogeneous catalysis. The exclusively high activity and selectivity brought by the unsaturated coordination sites and unique electronic structures of SACs render them promising materials for photocatalytic organic synthesis. In addition, well-defined single-atoms as active sites make the clear identification of reaction mechanisms possible. This has seen success in selective dehalogenation reactions,^[64] and we expect further progress could be made in photocatalytic oxidation reactions. SAC photocatalyst is not the topic of this review and the interested audience is proposed to read a recently published review.^[65]

3.3. Hybrid Materials

Hybridizing non-metal components such as carbon-based materials or metal oxides with photocatalysts can take advantage of the unique properties of different materials, providing researchers a powerful toolkit to manipulate the light harvesting, adsorption ability, and ultimately the activity and selectivity of photocatalysts. Moreover, the formed internal electric field arising from the suitably matched band structures could promote the transfer of photogenerated charge carriers, facilitating the charge separation.

Like metal loading, the early work encompassing hybrid materials focused on TiO₂-based catalysts. For example, a composite catalyst combining multi-walled carbon nanotubes (CNT) and TiO₂ was prepared using a modified acid catalyzed sol-gel method.^[66] When applying this catalyst for phenol oxidation, broadened absorption was observed, especially in the visible spectral range. Further investigation indicated that the activation of near-UV to visible light irradiation was due to a synergy effect: CNT acting as a photosensitizer agent instead of an adsorbent or a dispersing agent. In parallel, reduced graphene oxide (rGO) hybridized TiO₂ was found to catalyze photooxidation of cyclohexane to cyclohexanone with enhanced activity and selectivity under UV light ($\lambda > 300$ nm).^[31c] The TiO₂/rGO hybrids generated cyclohexanone two times higher than the amount produced on bare TiO₂, also with a much higher selectivity (>80%) than that of bare TiO₂ (~60%). Mechanism analysis showed that the photoactivated electrons in the TiO₂ CB band could transfer to rGO, facilitating efficient charge separation and enhancing photocatalytic activities (Figure 7). The trapped electrons on rGO selectively promoted the activation of O₂ via two-electron reduction and suppressed one-electron reduction. This process could largely inhibit the generation of $\cdot\text{O}_2^-$, which was responsible for the photocatalytic decomposition of formed cyclohexanone. In this way, rGO could effectively accelerate selective oxidation of cyclohexane on the hybrid catalyst. Readers interested in graphene related hybrid photocatalysts are kindly referred to another review dedicated to this field.^[67]

TiO₂ can also be hybridized with other metal oxides, leading to the adaptation of semiconductor junction architecture. For example, TiO₂ particles loaded with WO₃ were used for alcohol

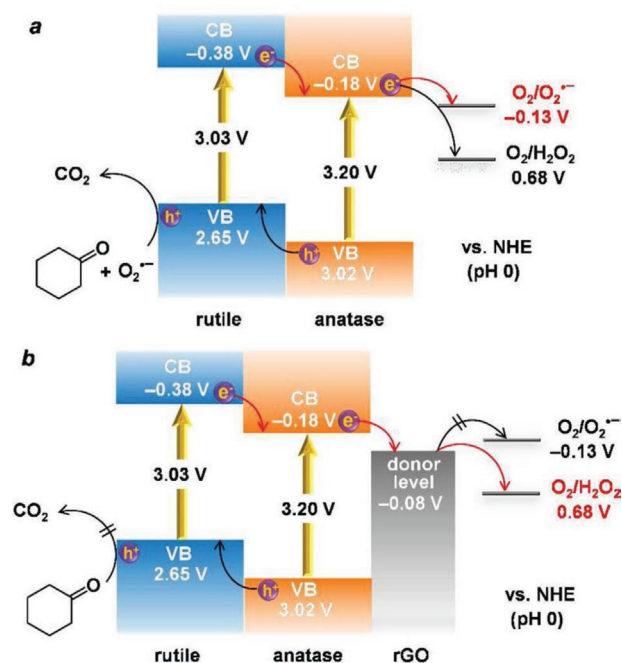


Figure 7. Energy Diagrams for a) TiO₂ and b) TiO₂/rGO when used in selective cyclohexane oxidation. Reproduced with permission.^[31c] Copyright 2017, American Chemical Society.

oxidation in water in the presence of O₂ and $\lambda > 350$ nm light.^[68] The WO₃/TiO₂ hybrid catalyst could selectively oxidize alcohols into aldehydes at a higher catalytic activity and selectivity than bare TiO₂. The enhanced selectivity to aldehyde was attributed to the inhibition of photocatalytic decomposition of the formed aldehyde on the catalyst. When partially coating TiO₂ by WO₃, the adsorption ability of aldehyde by TiO₂ was weakened, thus suppressing subsequent photocatalytic decomposition of aldehyde on the TiO₂ surface and thus achieving high selectivity.

The rapid development of controllable fabrication of nanocomposites has brought new light to highly active photocatalyst fabrication. Among them, the core-shell nanocomposites are particularly interesting due to their novel properties. TiO₂ nanofibers with a single-crystal TiO₂(B) core and a shell of anatase nanocrystals were produced and then applied to the alcohol oxidation.^[69] Meanwhile, Ce³⁺ ions were introduced into the (110) lattice planes of the TiO₂(B), in which the redox potential of Ce³⁺/Ce⁴⁺ couple (1.715 V versus NHE) was more negative than the VB of TiO₂(B). Therefore, the doped Ce³⁺ ions could collect photogenerated holes, leaving electrons in anatase shell and leading to a highly efficient charge separation. This may increase the chance for the activation of O₂ molecules adsorbed on the anatase surface, thereby improving the photocatalytic activity. Moreover, these doped ions can effectively trap the highly oxidative holes; thereby, overoxidation of the alcohol could be avoided.

In addition to the extensively studied TiO₂, CdS, a semiconductor with a narrower bandgap, has also been widely used as a component in hybrid photocatalyst for organic oxidation. Taking core-shell structured CdS@CeO₂ composite (with CeO₂ as the shell layer) as an example, this hybrid photocatalyst was used in the oxidation of benzyl alcohol.^[70] Apart from

the enhanced charge separation, the redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$ in CeO_2 shell could also transfer the electrons from the inner layer of CeO_2 shell to its outer layer. As the photoactivation of CdS core was also very important, the transmittance and charge transferring capacity to the outer component were quite important for core-shell photocatalysts. Another successful case is the porous $\text{Cd}_3(\text{C}_3\text{N}_3\text{S}_3)_2$ and CdS composite, which was employed for selective oxidation of toluene under visible light ($\lambda > 420 \text{ nm}$).^[71] The high selectivity was closely related to the proper band position of the two components: the CB of CdS was sufficiently negative to reduce O_2 and the VB of $\text{Cd}_3(\text{C}_3\text{N}_3\text{S}_3)_2$ was inadequate to oxidize OH group to $\cdot\text{OH}$ radicals. Meanwhile, the heterojunction structure could promote charge separation and boost the yield of benzaldehyde.

In 2018, photochromic $\text{Bi}_2\text{WO}_{6-x}$ /amorphous BiOCl (*p*-BWO) nanosheets have been discovered to be an efficient material for the oxidation of benzylic C–H bonds in toluene.^[31d] The hybrid nanosheets could become blue under visible light irradiation and be bleached by atmospheric oxygen. Further investigation revealed that photoactivated electrons could reduce $\text{W}_{(\text{VI})}$ into $\text{W}_{(\text{V})}$, and $\text{W}_{(\text{V})}$ could be oxidized by O_2 to regenerate $\text{W}_{(\text{VI})}$. Therefore, the introduction of amorphous BiOCl provided abundant $\text{W}_{(\text{VI})}\text{O}_{6-x}$ units, which could serve as the centers for the fast and continuous consumption of photogenerated electrons, thereby effectively promoting the separation of charge carriers.

More recently, MXenes, a new family of 2D transition metal carbides, carbonitrides, or nitrides have become a promising material to construct hybrid photocatalysts. Their strong light absorption ability, low Fermi level, and electrical conductivity render them an ideal cocatalyst to broaden light absorption and collect electrons in the composite catalyst. In organic synthesis, a low-temperature wet chemistry process was proposed to fabricate uniformly distributed CdS nanoparticles on the 2D platform of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets.^[72] The composites showed a significant enhancement in the aqueous photoredox conversion of furfural alcohol to furfural and H_2 by simultaneously utilizing photogenerated holes and electrons. Here, MXene nanosheets acted as an “electron sink”, facilitating the separation and transport of electrons activated in CdS nanoparticles. Electrons accumulated in MXene nanosheets then initiated the H_2 generation reaction. Meanwhile, the photoactivated holes in CdS nanoparticles oxidized furfural alcohol into value-added furfural, thereby completing the catalytic cycle.

Covalent organic frameworks (COFs), in which building blocks are connected through covalent bonding, have emerged as an exciting class of crystalline porous polymers and have been successfully applied in photocatalytic reactions.^[73] For example, highly hydrophilic COF material TFPT-BMTH, with high crystallinity and good chemical stability, exhibited significant catalytic activity in photocatalytic oxidation of benzylamine in water under visible light.^[74] However, the rapid recombination of photoactivated charge carriers is a main inhibiting factor for COFs to display excellent catalytic performance. Taking advantage of their large surface area and abundant functional groups, MOFs could be ideal platforms to hybridize with COFs, forming heterostructures and thus improving the photocatalytic ability. A successful case is the covalent-connected $\text{NH}_2\text{-MIL-125@TAPB-PDA}$ nanocomposite.^[75] The results

showed that hybridizing MOF and COF through covalent bonding could effectively extend the light absorption band and reduce the recombination rate of photogenerated charge carriers. When testing for benzyl alcohol oxidation, the hybrid showed a 15.5 times improvement in conversion compared with bare TAPB-PDA and remained stable after 5 cycles. Thus, the hybrid strategy has shown tremendous potential in the optimization of MOF and COF materials as photocatalysts.

3.4. Defect Engineering

Defects can naturally exist or be artificially created in materials. The defects in semiconducting photocatalysts can change band gaps to improve light absorption, serve as active sites to separate photoactivated electron-hole pairs, and participate in molecular chemisorption with a significantly reduced energy barrier. By virtue of the progress in material preparation methods and newly developed characterization technologies (especially aberration-corrected high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) and X-ray absorption spectroscopy), the past decade has seen a huge leap in the defects engineering for photocatalytic materials. Various kinds of defects, including vacancies, dislocations and structural distortions, have been introduced and proved to be an effective strategy for enhancing the efficiency and selectivity of photocatalytic oxidation reactions.

It is well-known that the chemisorption plays a critical role in photocatalysis, which not only facilitates the transfer of photoactivated charge carriers to reactants but also changes the formation of ROS to achieve an excellent selectivity. To promote the chemisorption of O_2 molecules on the surface of a photocatalyst, defect-rich WO_3 nanosheets were investigated for aerobic oxidation of amines to corresponding imines.^[76] HAADF-STEM images revealed that the sample surface contained numerous small dots. Concomitant with these dots, lattice disorders and dislocations were found inside of the nanosheets. These dots were considered as defect sites, which could enhance the chemisorption of molecular O_2 to the WO_3 surface. Moreover, they favored the transmission of photoexcited electrons to adsorbed O_2 , forming superoxide radicals in a chemisorbed state ($^*\text{O}_2^-$). The $^*\text{O}_2^-$ radicals possessed the identical oxidative capacity to free $\cdot\text{O}_2^-$, meaning they could react with the hole-activated substrate molecules located at the neighbored O atoms. In this way, photoexcited electrons and holes could be well-separated at different sites. Because the energy to create $^*\text{O}_2^-$ was relatively lower than $\cdot\text{O}_2^-$, small photon energy could be utilized. Therefore, the aerobic oxidation of amines to corresponding imines at room temperature could efficiently proceed under visible-near-infrared illumination.

While optimizations of chemisorption and charge separations have been regarded as the most effective strategies for the regulation of charge carrier generation in photocatalysts, some researchers devoted to the excitonic aspects of photocatalysts. An exciton, widely exists in semiconductors, is a bound state of electron-hole pair attracted by the electrostatic Coulomb force. Therefore, the dissociation of excitons into free charges would be a promising strategy for charge carrier utilization in photocatalysis. Because excitons are preferential to dissociate

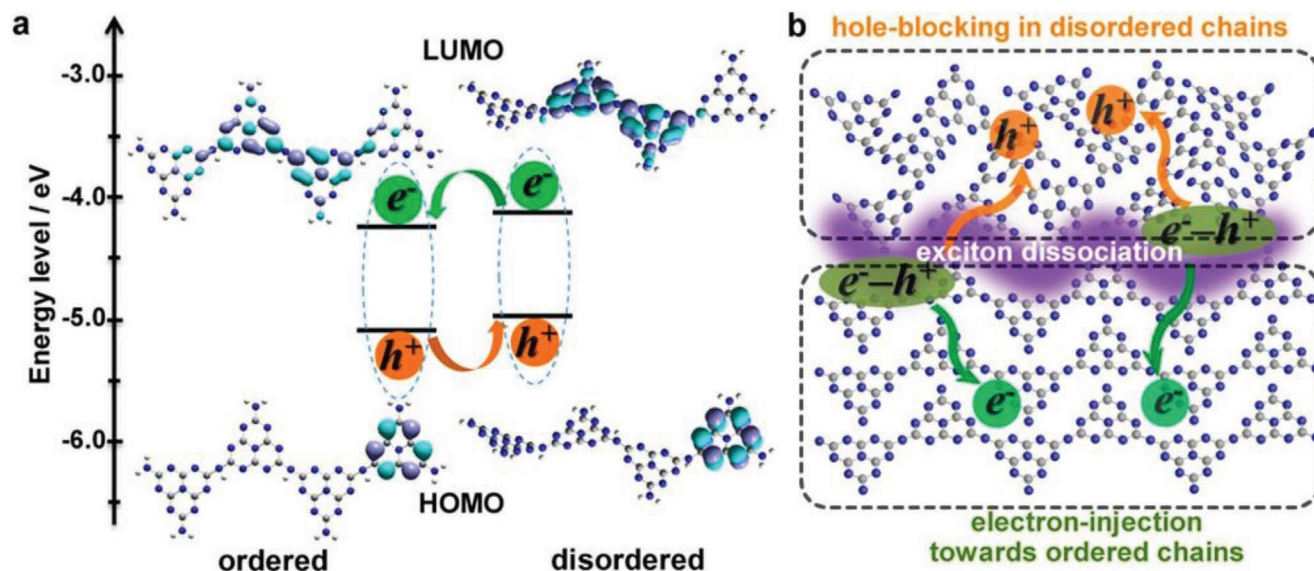


Figure 8. a) DFT simulations of ordered and disordered heptazine-based chains. Inset: corresponding charge-carrier transfer behaviors (blue balls, nitrogen atoms; gray balls, carbon atoms). b) Schematic illustration of exciton dissociation and charge transfer in semicrystalline heptazine-based melon. Adapted with permission.^[77] Copyright 2017, American Chemical Society.

into hot electrons and hole at the area with a disordered energy landscape, introducing disordered regions should improve the utilization efficiency of the excited charges. From this point, carbon nitrides with abundant order–disorder interfaces have been thoroughly investigated in which the enhanced hot-carrier generation was observed.^[77] Density functional theory (DFT) simulations revealed lower highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of ordered domains compared with the energy levels of disordered domains (**Figure 8**). This means hot electrons could be injected into ordered chains and holes could be blocked in disordered chains. Benefiting from this unique structure, the sample exhibited largely enhanced $\cdot\text{O}_2^-$ radical generation and improved selective alcohol oxidation.

Point defects, including various kinds of vacancies, are also frequently introduced in selective oxidation reactions. For example, introducing oxygen vacancies (OVs) into Au loaded BiOCl would trap hot electrons generated in plasmonic Au nanoparticles.^[29] Moreover, OVs can enhance the adsorption ability to O_2 molecules, reducing them into $\cdot\text{O}_2^-$ radicals. Together with the mild oxidative ability of hot holes, this photocatalyst highly favored the generation of benzaldehyde along with an exceptional oxygen atom transfer from O_2 to the product. Likewise, In another case, cubic indium sulfide ($\beta\text{-In}_2\text{S}_3$) was chosen as a model system and introduced surface S vacancies.^[30] DFT calculations revealed an obviously increased density of states at the VB maximum in In_2S_3 after the introduction of S vacancies (**Figure 9**). This means the electrons could be photoexcited to the CB and transferred to the defective surface more efficiently, thus suppressing electron-hole recombination. Moreover, the S vacancy site had a negative adsorption energy of -0.31 eV with molecular O_2 , while pristine In_2S_3 showed no obvious interactions. These properties made In_2S_3 with S vacancies an ideal material to efficiently generate $\cdot\text{O}_2^-$ radicals. Together with the photoactivated holes, this catalyst showed

excellent performance for photocatalytic benzylic alcohols oxidation reactions under visible-light irradiation.

Except for bulk materials, vacancies could even be introduced in some 2D materials. Although this is far more challenging because of the ion/defect migration. Interestingly, unit-cell Bi_2WO_6 monolayer was reported to provide a suitable model for this task as W-site defects in the interior WO_4 layer were relatively stable. In this context, interior W vacancies rich Bi_2WO_6 monolayers were prepared and found to be an efficient photocatalyst for benzylic alcohols oxidation.^[78] Under illumination, photoactivated holes in the $[\text{BiO}]^+$ surface layers could oxidize benzyl alcohol while electrons in the $[\text{WO}_4]^{2-}$ layer experienced a long migration toward the edge of the catalyst to reduce O_2 . W vacancies introduced mid-gap states into the defect Bi_2WO_6 , making electrons more easily excited by low-energy photons. This explained the enhanced visible absorption and higher photoconversion efficiencies.

With the suitable introduction of vacancies, some polymer materials could also be applied in selective alcohol oxidation. For example, nitrogen vacancies were introduced into the framework of carbon nitrides by a high-temperature thermal condensation method.^[79] In the resultant material, the nitrogen vacancies were grafted on the uncondensed terminal NH_x lattice sites, which lead to the improvement of the photogenerated charge carrier separation. When used in photocatalytic selective oxidation of aromatic alcohols, the catalyst achieved 68.3% benzyl alcohol conversion and almost 100% selectivity under simulated sunlight irradiation.

Studies on benzene and amine oxidation also explored the potential benefits of the vacancies in photocatalysts. Zn_2Ti -layered double hydroxide was used for selective oxidation of benzene to phenol in water.^[80] The abundance of oxygen vacancies improved charge separation and $\cdot\text{O}_2^-$ generation, resulting in the excellent catalytic performance under Xe lamp irradiation. When using ultrathin HNb_3O_8 nanosheets

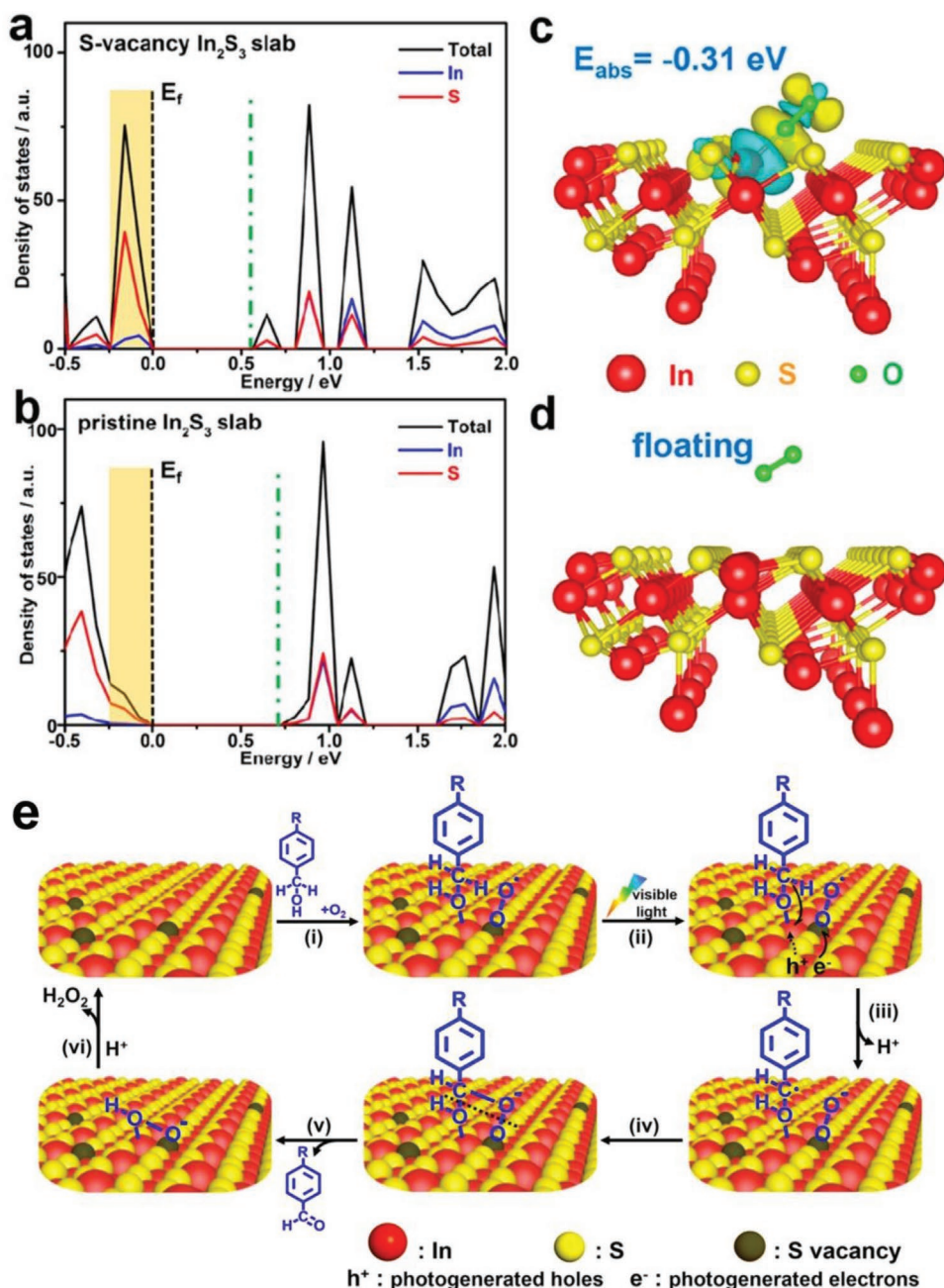


Figure 9. Calculated DOS of a) S-vacancy and b) pristine In_2S_3 slabs (E_f = Fermi level; orange shading marks the increased DOS around the VBM). c) O_2 interacts with the S vacancy in the defective In_2S_3 slab. d) O_2 floating on the surface of the pristine In_2S_3 slab. e) Proposed mechanism of photo-oxidation of benzyl alcohol to benzaldehyde over defective In_2S_3 . Adapted with permission.^[30] Copyright 2019, American Chemical Society.

with abundant oxygen vacancies in the photocatalytic oxidative coupling reaction of benzylamine, enhanced performance under visible light irradiation was observed.^[81] Benzylamine was preferentially adsorbed on the O vacancies on HfNb_3O_8 , forming a surface complex. It has been proved that this surface complex could reduce the bandgap of HfNb_3O_8 , making the material responsive to the visible light. Under irradiation, photogenerated holes reacted with adsorbed benzylamines to form the corresponding nitrogen-centered radicals. Simultane-

ously, photogenerated electrons activated O_2 into $\text{O}_2^{\cdot-}$ at the same site. After a series of reactions, the resultant intermediates could be converted into imines. In another paper, Bi_2WO_6 containing Au nanoparticles and oxygen vacancies was applied for the same reaction.^[82] The role of O vacancies for efficient adsorption-activation of molecular O_2 has been verified in this work. Moreover, the existence of Au nanoparticles further boosted the generation of hot electrons, therefore resulting in the enhanced photocatalysis.

3.5. Morphology and Crystallization Control

Through manipulating the morphology of photocatalysts, the selectivity could be promoted in organic oxidation reactions. As described in Section 2.3.3, benzene could be oxidized by the $\cdot\text{OH}$ radicals formed on the photoexcited semiconductors, surface. The formed phenol is, however, subsequently attacked by $\cdot\text{OH}$ radicals, leading to a low phenol selectivity. This problem could be solved by using mesoporous TiO_2 particles ($m\text{TiO}_2$) prepared through the surfactant-templating method or particle aggregation method.^[83] Because benzene are less polar molecules, they tended to adsorb on the less polar inner surface of $m\text{TiO}_2$. After they were converted into polar phenol, they were hardly adsorbed onto the $m\text{TiO}_2$ surface. Photogenerated $\cdot\text{OH}$ radicals inside the pores of $m\text{TiO}_2$ were said to be converted to inactive surface OH groups in a near-diffusion controlled rate and they scarcely diffused out of the pores. Therefore, $\cdot\text{OH}$ radicals could well-react with adsorbed benzene and leave phenol intact, resulting in highly selective oxidation (81% selectivity). Soon after this, the same group further verified this adsorption-driven photocatalysis strategy by employing microporous titanosilicate ETS-10 (Engelhard Titanosilicate Structure 10) for the same reaction.^[84]

Modifying morphologies can not only alter the adsorption behavior of substrates, separation of photogenerated charge carriers could also be promoted in some cases. Sheet structured semiconductor CdS with a cubic phase was demonstrated to selectively oxidize C–H bonds under visible light irradiation in toluene.^[85] Although the authors could not give a plausible explanation for the enhanced activity and selectivity of resultant catalyst, they showed that the crystalline phase, surface area and particularly morphology all had an important impact on photocatalytic activity. These factors would result in different geometric and electronic structures in catalysts, thus endowing them with excellent photocatalytic performance. A similar phenomenon was also observed in single-crystalline BiOCl ultrathin nanosheets with a square morphology.^[86] Additionally, distinctive from the nanoplates prepared by the hydrothermal route, BiOCl ultrathin nanosheets featured the hydrophobic surface, which could be beneficial to the selective oxidation of amines.

The rapid development in the synthesis of advanced low-dimensional materials has brought more remarkable semiconducting materials as photocatalysts. Sometimes these newly developed photocatalysts demonstrate intriguing properties. For instance, Ultrathin black phosphorus (BP) nanosheets exhibited an excitation-energy-dependent effect in photocatalytic ROS formation.^[87] Interestingly, $^1\text{O}_2$ and $\cdot\text{OH}$ could be almost exclusively generated under visible- and UV-light irritations, respectively. In-depth analysis revealed that there were two different subband systems in the ultrathin BP nanosheets, making it feasible for the energy-transfer and charge-transfer processes to proceed in different subband structures (Figure 10). Subband structures, resulting from giant electron–electron interactions and specific band dispersions, had mainly been observed in 1D materials including single-wall carbon nanotubes. Under visible-light irradiation, the resonance energy transfer from the excited excitons of BP in its inner subband system to the ground-state oxygen promoted the generation of $^1\text{O}_2$. When irradiated with UV light, photogenerated holes in the outer

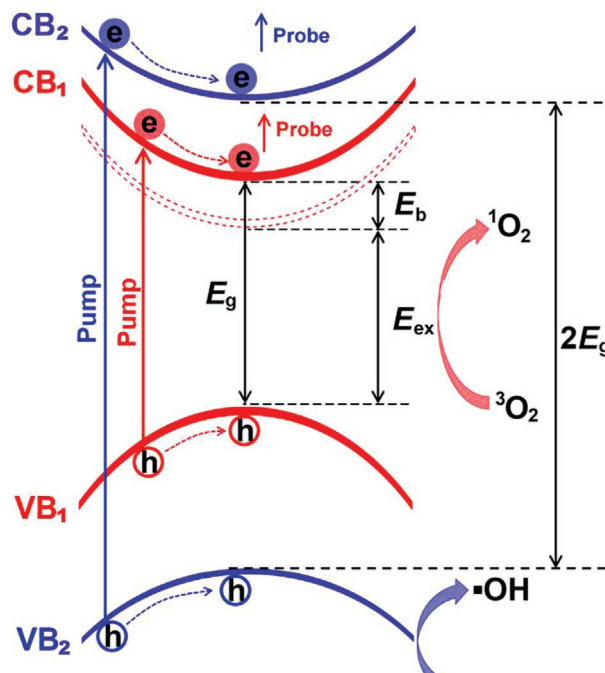


Figure 10. Schematic illustration of the subband structure of ultrathin BP nanosheet as well as the photoexcitation and photocatalytic processes occurring therein. The optically switchable ROS generation of $^1\text{O}_2$ and $\cdot\text{OH}$ are depicted corresponding to the internal and external band systems, respectively. CB_n and VB_n ($n = 1, 2$) denote the n th conduction band and valence band, respectively. E_{ex} and E_{b} stand for the excitonic energy level and exciton binding energy, respectively. Reproduced with permission.^[87] Copyright 2018, American Chemical Society.

subband system oxidized water into $\cdot\text{OH}$ radicals. This novel optically switchable property has shed new light on the photocatalysis research and could be potentially applied in the selective oxidation reactions because of controllable ROS generation.

Besides the manipulating of morphologies, subtly tuning the crystallizations of photocatalysts could be an alternative way to increase photocatalytic efficiency. This is particularly important for polymer materials, because the extended π -conjugated system and strong van der-Waals interactions between interlayers both benefit the charge transport.^[88] For inorganic materials, pioneering researchers extensively studied the different phases of TiO_2 , providing rich understandings for its application in selective oxidation. For example, anatase TiO_2 exhibited excellent activity for oxidation, though the desorption of target chemicals is sluggish.^[34] In most cases, the higher degree of crystallization means more efficient separation of charge carriers. However, less-crystalline rutile TiO_2 exhibited a higher selectivity in alcohol oxidation.^[89] The enhanced selectivity was attributed to the facilitated charge recombination, and consequently the restricted generation of strong oxidative $\cdot\text{OH}$ radicals. Additionally, OH groups formed from deactivated $\cdot\text{OH}$ radicals were favored to adsorb on the less-crystalline catalyst, forming a more hydrophilic surface. Desorption of resultant aldehydes was therefore improved, so was their selectivity. We believe this worked as a sacrifice of the conversion rate.

In recent years, lead-free halide perovskites with ABX_3 stoichiometry (where A = monovalent cation, B = In^{3+} , Bi^{3+} , Sb^{3+} ,

or Sn^{3+} , X = halide anion) have been demonstrated to be promising photocatalysts because of their appropriate bandgap and remarkable charge transfer properties. Modification of X-site and B-site ions can alter their band positions therefore control the light absorption and redox abilities. Although A-site ions are not involved in the formation of band gaps, they can cause octahedron distortions in the perovskite structure. This effect has been proved by using $\text{Cs}_3\text{Sb}_2\text{Br}_9$ nanoparticles in photocatalytic toluene oxidation to benzaldehyde.^[31e] The results showed the octahedron distortion induced by A-site cations led to the enhanced ability of hole transfer from Br sites to toluene molecules. Together with the generation of $\cdot\text{O}_2^-$ radicals, benzaldehyde molecules were efficiently formed at high selectivity. Because Br atoms on the surface were responsible for the formation of holes, and the octahedron distortion significantly affected its electronic properties, modification of A-site cations had a prominent effect on the photocatalytic efficiency in $\text{C}(\text{sp}^3)\text{-H}$ bond oxidation.

3.6. Surface States Manipulation

In photocatalytic reactions, the adsorption and oxidation of reactants, and the desorption of target chemicals all occur on the surface of photocatalysts. Therefore, the surface states largely affect the performance of the catalysts. Up to date, various surface states modification methods have been developed to tailor the surface characters. For example, the effect of silylation on the photocatalytic activity of anatase TiO_2 catalyst was investigated in selective cyclohexane oxidation.^[90] The yield of cyclohexanone was closely related to the abundance of surface active OH sites and the desorption rate of cyclohexanone. Silylation to an appropriate extent could improve the desorption of cyclohexanone; thereby, the selectivity was increased. Also due to the facilitated desorption rate, the formation of surface deactivating carbonate and carboxylate species on TiO_2 was suppressed. Meanwhile, another strategy to modify anatase TiO_2 has been proved to be feasible: clean the catalyst surface to expose active OH sites as much as possible.^[91] This could be achieved through pretreating anatase with different Brønsted acids. Surface modification of TiO_2 with both inorganic and organic acids significantly accelerated the oxidation of alcohols under irradiation of UV light at room temperature, without any compromise of selectivity compared to the untreated TiO_2 . This unique proton cleaning effect was attributed to the promotion of decomposition of the surface Ti/peroxide species and regeneration of Ti sites in the selective oxidation of alcohols. A similar cleaning strategy has also been applied in Nb_2O_5 photocatalysts for the oxidation of aromatic hydrocarbons—the treatment even broadened the photocatalytic absorption to the visible region.^[92] It turned out that the vacuum heat treatment enhanced the electron transfer between the aromatic ring and Nb_2O_5 surface, which served as an electron donor and an electron acceptor, respectively. This could initiate the absorption of visible light ($\lambda > 390$ nm) due to the ligand-to-metal charge transfer (LMCT) transition (Figure 11). Selective photooxidation of aromatic hydrocarbons to corresponding carbonyls could therefore be effectively facilitated under visible light irradiation. Interestingly, similar treatment did not lead to the same

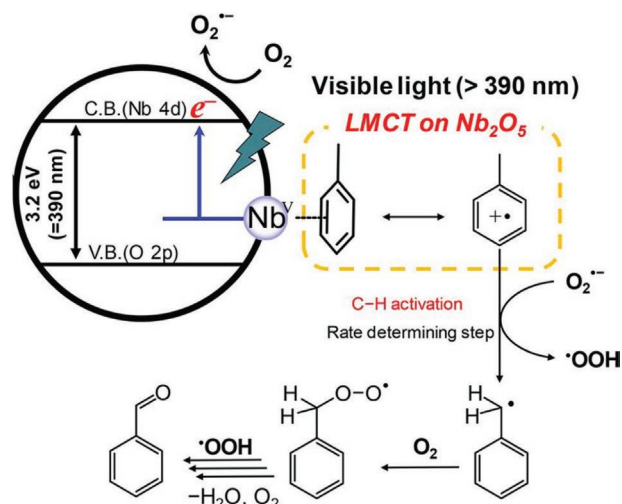


Figure 11. Proposed mechanism of visible-light photooxidation of aromatic hydrocarbons via a ligand-to-metal charge transfer (LMCT) transition on the surface of Nb_2O_5 after vacuum heat treatment. Reproduced with permission.^[92] Copyright 2017, American Chemical Society.

phenomenon on TiO_2 , which might result from the weaker electron-accepting ability of TiO_2 .

Compared with inorganic materials, the polymer photocatalysts have brought great opportunities to graft various functional groups on the surface and therefore potentially achieving optimal performance. For example, the oxidized CN was reported to significantly boost the generation of triplet-exciton.^[93] While enhancing the generation of $^1\text{O}_2$, the production of other ROS was concomitantly suppressed, rendering it an excellent material in $^1\text{O}_2$ -demanding organic synthesis. The remarkable difference in ROS generation properties between oxidized CN and untreated one was due to their distinct excitonic behaviors. Electron spin resonance (ESR) measurements revealed that oxidizing CN incorporated abundant carbonyl groups, which could synergistically promote spin-orbit coupling and reduce singlet-triplet energy gap of the matrix (Figure 12). Therefore, an efficient inter-system crossing (ISC) process was initiated, in which the excitons could readily transform from singlet excited state to lower-energy triplet excited states, further transferring energy to ground-state oxygen molecules to generate $^1\text{O}_2$. In another case, cyano groups were introduced onto the surface of CN nanosheets via a facile thermal post-treatment, which constructed a homojunction-like structure.^[94] This structure could efficiently facilitate the generation of charge carriers, thus promoting the formation of $\cdot\text{O}_2^-$ radicals. This photocatalyst was employed in the oxidative coupling of diverse amines to corresponding imines under $\lambda > 420$ nm light and achieved 2.4 times higher activity than pristine CN.

4. Conclusion and Perspectives

Although it is environmentally friendly, operated under very mild conditions and sustainable, the application of selective photocatalytic oxidations presents far more difficulties and challenges compared with other applications such as complete decomposition of organics in environmental protection.

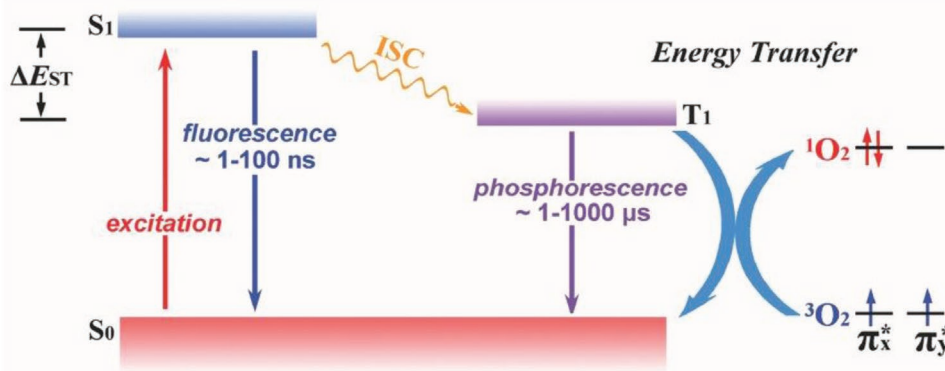


Figure 12. Illustration of the typical excitonic processes in the conjugated structure and the energy transfer process for $^1\text{O}_2$ generation. Reproduced with permission.^[93] Copyright 2016, John Wiley & Sons.

The key issue in selective oxidation is the control of ROS and adsorption-desorption behavior. The past few decades have seen substantial progress in the development of photocatalytic oxidations. In this critical review, besides the basic mechanism of photocatalysis, typical oxidation reactions are briefed, and key strategies to improve the selectivity as the focus of this review are detailed. In general, these strategies show positive effects on photocatalytic organic oxidations, such as broadening the region of light absorption, facilitating charge carrier separation and transport, and promoting reactant adsorption and activation processes, all of which are crucial steps in photocatalytic processes as detailed in the above sessions. Despite the progress in the development and understanding of photocatalytic oxidations for organic synthesis, we believe there are three major challenges to overcome in this field.

The first challenge is to better understand the reaction kinetics the roles played by added defects. At present, the modification of photocatalysts to improve selectivity for a specific oxidation reaction relies on the tentative optimization case by case, since there are many knowledge gaps among the surface characteristics of a catalyst, properties of ROS, and specific substrate molecules. A precise and in-depth understanding of the roles played by each ROS in different reactions is extremely important. To this end, by virtue of valid characterization techniques such as ESR, various ROS involved in photocatalytic oxidation reactions have preliminarily been identified and their pivotal roles for photocatalytic activity improvement have in part been proposed. However, the existing techniques can only indicate the existence of ROS, which can hardly clarify the specific role of various ROS. In this sense, the precise characterization of ROS and clarification of their functions in photocatalytic processes remain challenging. Another species closely related to the mechanism of selective photocatalytic oxidation are the added defects. Most literature reported positive effects of the added defects in photocatalytic oxidations. Under certain circumstances, however, the defects may serve as charge carrier recombination centers during photocatalytic processes.^[95] A comprehensive understanding of the function played by defects is exceptionally significant in developing efficient photocatalysts. Benefited from the modern characterization techniques such as X-ray photoelectron spectroscopy and scanning transmission electron microscopy (STEM), various added defects in photocatalytic oxi-

dations have been identified and their roles for photocatalytic selectivity enhancement have been proposed. However, existing techniques can barely reveal the correlation of the concentration and local atomic environment of these defects with their activity, which is essential to understand their roles in diverse reactions. Establishing more advanced characterization techniques such as in-situ STEM/liquid transmission electron microscopy (TEM) is therefore critical to clarify the functions of added defects and to reduce their negative effects on selective oxidation.

A second challenge, closely connected to the first, is to in-situ observe reaction mechanism, involving the characterization of active sites and the transformation of intermediates during photocatalytic reactions. Although the theoretical calculation is a powerful method for the study of surface properties and reaction route of a catalyst, the simulated ideal models are to some extent hard to reflect the real environment and complexity of the reaction and adsorption-desorption behavior. Emerging techniques should be developed to characterize the active sites and to analyze catalytic mechanism, which is of great value for designing efficient photocatalysts. For example, using oxygen isotope to trace the source of O in the oxygenates, which has been proved to be an effective method to clarify the reaction routes during oxidation reactions.^[42] Operando characterizations, a series of cutting-edge techniques for revealing the catalytic reaction mechanism and the dynamic intermediates evolution under the conditions close to real reaction, should also be widely used in photocatalytic oxidations. It has received a substantial push in recent years, and unsurprisingly, generating a library of exciting results. For instance, coupling time-resolved IR and Raman spectroscopy with mass spectrometry could on-line identify species adsorbed on the photocatalyst surface, species in gas phase and subtle surface change of catalysts under “true” reaction conditions, leading to further clarification of the photooxidation mechanisms.^[96] Based on these solid experimental results generated from advanced characterization techniques, strong collaboration with modeling work is crucial to validate the model and predict effective strategy for material modification in a quasi-real condition.

The final challenge is developing more robust methods to realize the rational design of efficient photocatalysts. Further improving selectivity in photocatalytic oxidation raises a higher demand for catalyst synthesis. Taking Pt loaded TiO_2

as an example, the number of peripheral active sites is crucial to the formation of target compounds.^[55] Achieving a large amount of Pt nanoparticles and a tight particle size distribution was therefore beneficial to the selectivity of the alcohol oxidation reaction. Related to this, advanced methods for tailoring the electronic and chemical structures of photocatalysts should be developed. Specifically, single atomic-site catalysts (SACs) or atomic clusters, which could bring exclusively high activity and selectivity in photocatalytic organic synthesis,^[97] are still scarcely studied, which is probably because of difficulties in controlling SACs loading and their distinct characterization. Despite the extensive studies made to prepare single atomic-site photocatalysts, the synthesis of such SAC with a high content (>10 wt%) is still a major challenge. On the other hand, the selectivity of the most currently available SACs is unsatisfying because the single atoms are too active, readily reacting with surrounding reactants and thereafter forming undesired species. For these reasons, it is of significance to seek and develop new strategies to controllably synthesis SACs with high metal content in an appropriate circumstance. More importantly, SACs can offer us new opportunities for capturing the reaction intermediates at the atomic scale, and even monitoring the dynamic behaviors of both the geometric structure and electronic environment of the catalytic sites. Coupling the studies of SACs with operando techniques may lead to atomic-level identification of the dynamic structure of catalytically active sites and a deeper understanding on reaction mechanisms. This has seen success in Pt single sites on CeO₂,^[98] we expect further progress could be made in photocatalytic oxidation reactions.

The synthesis of organic chemicals has been studied for almost 200 years with many landmark achievements. Most of the industrial production of these organic chemicals are conducted under high temperature and elevated pressure, resulting in significant energy consumption and adverse environmental impact. Facilitating organic synthesis under light irradiation, might be under sunlight, and in a benign environment has been proved to be a feasible approach while still requiring vigorous and substantial investigation.

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Conflict of Interest

The authors declare no conflict of interest.

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