Organic & Biomolecular Chemistry

REVIEW

Cite this: *Org. Biomol. Chem.*, 2019, **17**, 9977

Recent advances in modified TiO_2 for photo-induced organic synthesis

Haojie Cheng[a] and Wentao Xu *[b]

Received 7th August 2019,
Accepted 31st October 2019

DOI: 10.1039/c9ob01739a

rsc.li/obc

Over the last decade, chemists have made great progress in photocatalysis. Compared with the well-developed homogenous photocatalysis for organic synthesis, heterogeneous photoredox catalysis is still in its infancy. In this review, we summarized the recent developments of TiO_2-based materials in heterogeneous photocatalysis for organic synthesis. Generally, modified TiO_2 shows enhanced photocatalysis with a narrow band gap or broad absorption spectrum. Based on the present work, the future perspectives of modified TiO_2 photocatalysts for organic synthesis are presented.

1. Introduction

Nowadays, the use of visible light as a renewable and green energy source can address energy crisis and environmental pollution.[1] To date, photocatalysis has been broadly applied in water splitting,[2] development of novel solar cells,[3] and organic synthesis.[4] During the past decade, homogenous photocatalysis has drawn tremendous attention in the area of organic synthesis; various metal complexes or organic dyes have been used as photocatalysts (Fig. 1).[4b] Although these catalysts show good catalytic activity in diverse reactions, they also suffer from several problems, such as high cost, difficulty of preparation, facile decomposition during the reaction, and recycling problems. In this context, heterogeneous photocatalysts[5] such as TiO_2 and modified TiO_2 photocatalysts appear to be promising choices. TiO_2 is commercially available and very inexpensive. Under the irradiation of UV light (λ < 387 nm), the electrons at the conduction band (CB) are available for reduction reactions, while the generated holes (h^+) in the valence band (VB) are usually involved in oxidative reactions. TiO_2 has a broad band gap (3.2 eV), which will lead to poor selectivity for organic synthesis. In order to avoid charge recombination, narrow the bandgap, and improve the light absorption, modified TiO_2 photocatalysts have been more commonly used in recent years.

A growing number of publications on photochemistry have emerged during the last decade. We limited our search to articles and reviews, and about 95 095 papers related to photocatalysis were collected (Fig. 2). As shown in Fig. 3, the results show that the development of photocatalysts and their application in photocatalysis are the main research topics. Indeed, different types of anatase TiO_2 have been prepared, characterized and applied in photochemistry. Interestingly, photoredox

---

[a] *School of Information Management, Nanjing University, Nanjing 210023, Jiangsu, China*
[b] *School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, Jiangsu, China. E-mail: wtxu@smail.nju.edu.cn*

Haojie Cheng

Haojie Cheng was born in Henan Province, China. She received her Bachelor's degree from Zhoukou Normal University in 2015 and her Master's degree from Tianjin Normal University in 2017. She is currently conducting her Ph.D. studies under the supervision of Prof. Qinjian Yuan at Nanjing University. Bibliometrics is her major research field.

Wentao Xu

Wentao Xu was born in Hubei Province, China. He received his Bachelor's degree from the Hefei University of Technology in 2014 and his Master's degree from the same university in 2017. He is currently conducting his Ph.D. studies under the supervision of Prof. Jin Xie and Prof. Chengjian Zhu at Nanjing University. His current research interest focuses on photoredox catalysis.

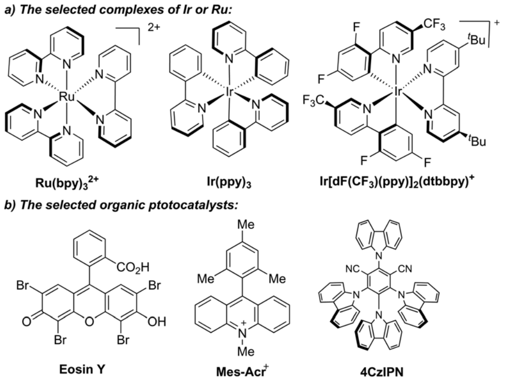


Fig. 1 Chemical structures of some homogenous photoredox catalysts.

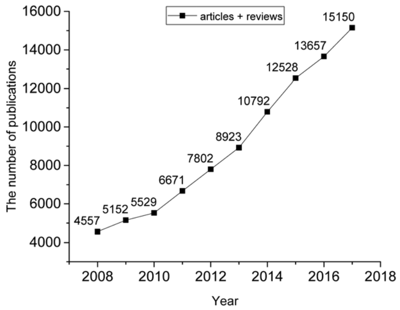


Fig. 2 The number of published papers on photocatalysis (2008–2017).

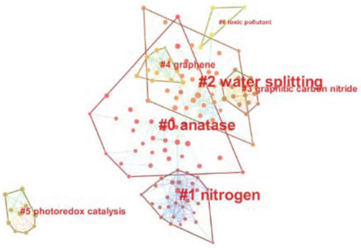
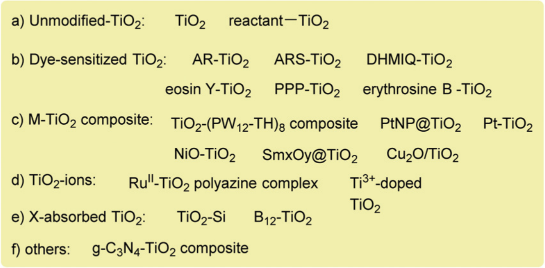


Fig. 3 A visualization of the document co-citation network.

catalysis is an independent field, which suggests that anatase TiO_2 may not be widely used in organic synthesis.

Although reviews related to the synthesis, properties, modifications, and applications of anatase TiO_2 have been published,[6] only a few reviews discuss the use of TiO_2 for organic synthesis.[7] Shiraishi selected several representative examples, in which TiO_2-based materials catalyzed organic transformations before 2008.[8] Recently, Bloh and Marschall focused on recent developments in materials, reactors, and reaction design in heterogeneous photoredox catalysis.[9] Yin mainly focused on the heterogeneous photocatalysis oxidation of alcohols and hydrocarbons.[5b] During the last decade, chemists have been paying increasing attention to modifying TiO_2 to develop synthetic chemistry. A large number of elegant studies have appeared. Hence, it is highly desirable and valuable to comprehensively review the recent significant progress in organic reactions catalysed by TiO_2-based materials.


a) Unmodified-TiO_2: TiO_2 reactant—TiO_2

b) Dye-sensitized TiO_2: AR-TiO_2 ARS-TiO_2 DHMIQ-TiO_2 eosin Y-TiO_2 PPP-TiO_2 erythrosine B -TiO_2

c) M-TiO_2 composite: TiO_2-$(PW_{12}\text{-TH})_8$ composite PtNP@TiO_2 Pt-TiO_2 NiO-TiO_2 SmxOy@TiO_2 Cu_2O/TiO_2

d) TiO_2-ions: Ru^{II}-TiO_2 polyazine complex Ti^{3+}-doped TiO_2

e) X-absorbed TiO_2: TiO_2-Si B_{12}-TiO_2

f) others: g-C_3N_4-TiO_2 composite

Fig. 4 The selected TiO_2 and modified TiO_2 catalysts.

In this review, we discuss the recent organic reactions catalyzed by TiO_2-based materials *via* light irradiation. Due to the poor selectivity and short absorption spectrum of TiO_2 (λ < 387 nm), a variety of modified TiO_2 materials have been synthesized to gain wider application scope in photoredox reactions (Fig. 4). Usually, these modified TiO_2 catalysts have sharp narrow band gaps or are able to absorb visible light. Based on the quenching mechanism of the photocatalyst, the reactions mainly include oxidative and reductive reactions. These reactions can be further divided into five major groups: (i) oxidative reactions, (ii) reductive reactions, (iii) addition reactions, (iv) cyclo(addition) reactions, and (v) cross-coupling reactions.

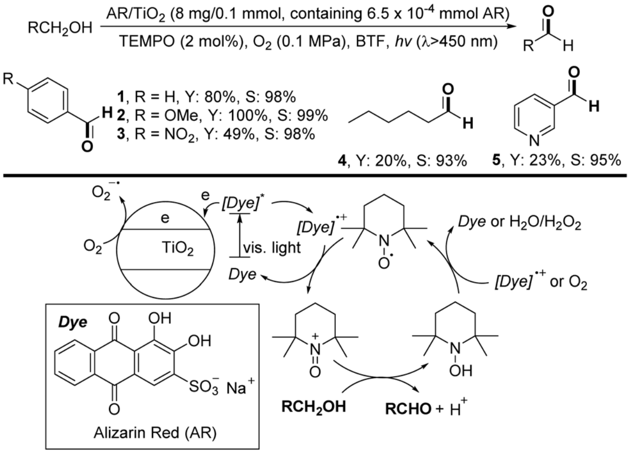
2. Oxidative reactions

2.1 Oxidation of alcohols

Alcohols, a class of significant chemicals, can be selectively oxidized to produce aldehydes. Traditional routes to aldehydes from alcohols usually involve transition-metal ions or deleterious oxidants. Heterogeneous photocatalysis is a good choice for these reactions.[5b]

In 2008, Ma and Zhao's group skillfully chose the excited dye Alizarin Red (AR) as an electronic medium and $TEMPO^+$ as an effective oxidant to accomplish selective oxidation of primary alcohols.[10] This strategy avoids indiscriminate oxidation because of the high oxidative potential of the excited TiO_2 (3.2 V). The catalytic cycle involves two key steps of electron transfer: (a) the excited dye delivers an electron to TiO_2 to produce a dye radical; (b) TEMPO is oxidated by the dye radical to generate $TEMPO^+$, which acts as a selective oxidant for alcohols to aldehydes. Generally, this reaction shows high selectivity (>93%), and substrates with electron-donating groups on the aromatic ring show better conversion (**1–3**). However, aliphatic (**4**) and pyridine (**5**) alcohols show low activity (Scheme 1).

Later, Zhao's group reported a significant breakthrough: that TiO_2 absorbed by a Brønsted acid could lead to considerable improvement in the photocatalytic oxidation of alcohols with high selectivity.[11] Especially, when TiO_2 was combined with a small amount of SiO_2, resulting in more Brønsted acid



Scheme 1 Aerobic oxidation of alcohols with the AR-TiO_2 catalyst.

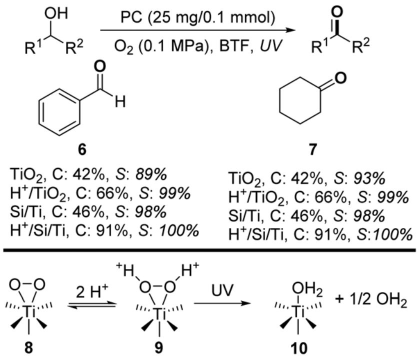
sites, the reaction afforded two-fold conversion. Taking benzyl alcohol and cyclohexanol as examples, a modified TiO_2 photocatalyst (H^+/Si/Ti) showed the best highest catalytic activation and selectivity (Scheme 2, **6** and **7**). The key point is that the absorbed proton can remarkably weaken the O–O bond to accelerate the decomposition of side-on peroxide (**9**) to afford **10**. The key intermediate **10** further undergoes selective oxidation of the alcohol to deliver the oxidation product.

Recently, Gao and Cao's group prepared a TiO_2-$(PW_{12}\text{-TH})_8$ composite (Scheme 3) and provided an alternative modified TiO_2 catalyst for oxidation of alcohols.[12] The screening of different photocatalysts (TiO_2-$(PW_{12}\text{-TH})_8$, P_{25}-$(PW_{12}\text{-TH})_8$, SiO_2-$(PW_{12}\text{-TH})_8$, $(TH)_3PW_{12}$ and TiO_2/TH) showed that the carefully prepared TiO_2 composite TiO_2-$(PW_{12}\text{-TH})_8$ had the highest effect on the conversion. When used in the reaction, it was found that high selectivity was achieved (**11–17**, >99%). However, heteroaromatics and alkyl alcohols afforded low yields (**14–16**), as did benzylic alcohols with increased steric hindrance (**17**).

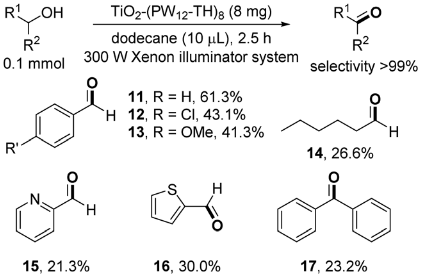
As a follow-up to the work of Ma and Zhao,[10] Lang and coauthors found that the ratio of TiO_2 and Alizarin Red S has a great effect on the catalytic oxidation (Table 1).[13] When ARS was used in a certain amount (1.33 mmol), the conversion sharply decreased due to the decrease of TiO_2 (entries 1–7). This catalytic strategy avoids using the organic oxidant TEMPO.

2.2 Oxidation of organic sulfides

In 2015, Chen's group reported aerobic oxidation of sulfides and amines to simultaneously produce two different products (**18**, **19**) on the surface of TiO_2 under visible-light irradiation.[14] When phenylmethanamine was used, the substituted thioanisoles with electron-donating groups and electron-withdrawing groups could be successfully transformed into the corresponding sulfoxides with high selectivities (**20–22**, **24**), except for the nitro group (**23**); however, a diphenyl sulfide showed relatively low activity (**25**). Meanwhile, *N*-benzylformamide was obtained with good selectivity. On the other hand, a number of substituted benzylamines are also compatible in the reaction (**26–31**), including heteroatom-containing benzylamines (**29–31**), in relatively low selectivity. In addition, secondary benzylamines could not afford the corresponding products because of their low reactivity with HCHO. The mechanism starts from the generation of a surface complex **32** on the surface of TiO_2 with the benzylamine, where the conduction band of TiO_2 absorbs an electron from the benzylamine to form intermediate **33**. Single electron transfer from the thioanisole to the amine cationic radical regenerates the benzylamine and delivers the thioanisole radical cation **34**, which subsequently reacts with O_2, replenishing the Ti^{IV} state. Then, subsequent electron and proton transfer complete the photoredox catalytic cycle, producing the desired products.

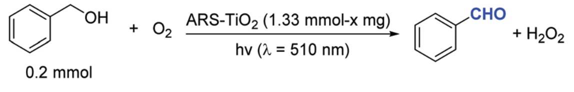


Scheme 2 Aerobic oxidation of alcohols with the TiO_2/Si catalyst.

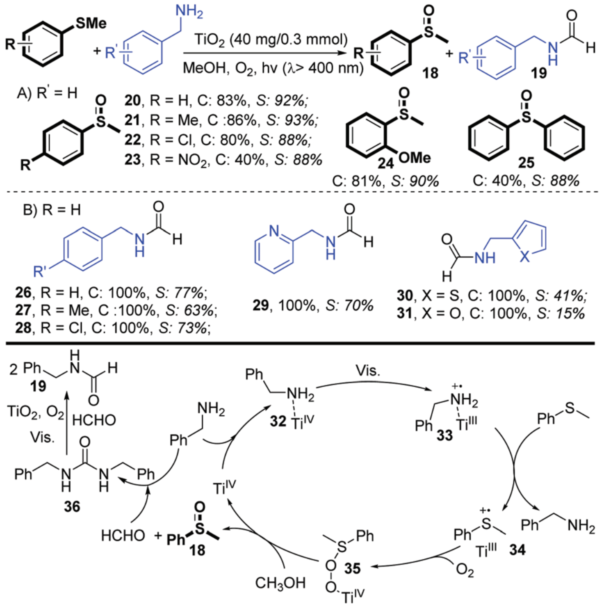


Scheme 3 Aerobic oxidation of alcohols with the TiO_2-$(PW_{12}\text{-TH})_8$ composite.

Table 1 The influence of the amount of TiO_2 on the aerobic oxidation of benzyl alcohol



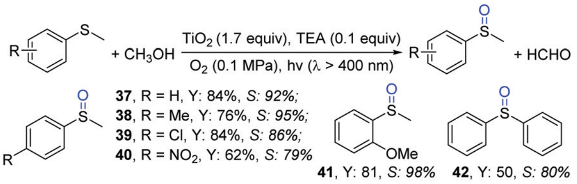
Entry	TiO_2 (mg)	Conversion (%)	Selectivity (%)
1	106.6	80	98
2	53.3	67	98
3	26.6	40	98
4	17.7	28	98
5	13.3	22	98
6	6.6	10	98
7	4.4	5	98



Scheme 4 The selective aerobic oxidation of sulfides and benzylamine on TiO_2.

Meanwhile, the produced HCHO can efficiently react with benzylamines to generate intermediate **36**, which undergoes its own decomposition to afford **19** in the presence of HCHO (Scheme 4).

Later, the same group disclosed a synergistic photoredox and organocatalysis reaction for the selective oxidation of sulfides to sulfoxides using TiO_2 as a photocatalyst.[15] In order to decrease the complexity of the reaction, triethylamine (TEA) was used instead of the well-developed primary benzylic amines.[14] The substituted thioanisoles with electron-donating groups and electron-withdrawing groups could be successfully transformed into the corresponding sulfoxides with high selectivities (**37–41**), while diphenyl sulfide showed relatively low activity (**42**). The mechanism is similar to their previous work. Note that no amides are formed in this reaction because TEA cannot react with HCHO (Scheme 5).



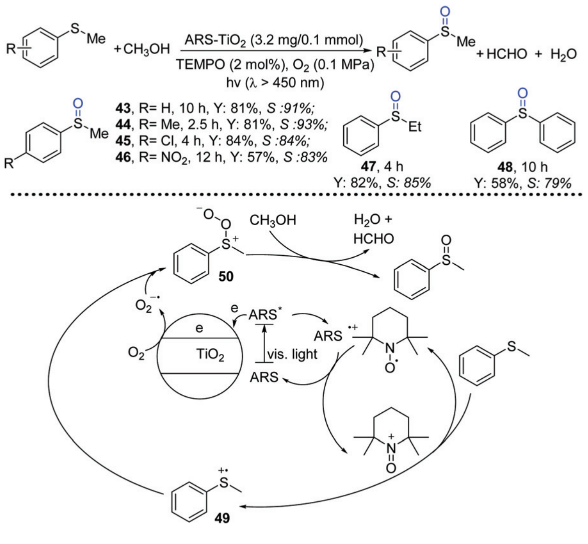
Scheme 5 Selective oxidation of sulfides into sulfoxides catalyzed by TiO_2 with TEA as a redox mediator.

In 2016, organic dye ARS-sensitized TiO_2 was found to be able to catalyze the oxidation of sulfides to sulfoxides using O_2 as the oxidant and TEMPO as the redox mediator.[16] The control experiments of the reaction showed that TEMPO, ARS, and O_2 are the keys to the success of the selective oxidation reaction. Also, TEMPO can ensure the stability of ARS on the TiO_2. In the reaction, thioanisole and its derivatives can be effectively transformed into the desired products (**43–48**). The mechanism starts from the excited ARS, which donates an electron to the conduction band of TiO_2, generating the ARS radical cation; then, the electron reacts with O_2 to produce O_2 radical anion. TEMPO, as a redox mediator, undergoes SET with the ARS radical cation to deliver $TEMPO^+$ and regenerate the dye ARS. $TEMPO^+$ reacts with thioanisole to afford the S-centered free-radical cation **49**, which prefers to react with O_2 radical anion to afford sulfide peroxide **50**. Finally, the sulfide peroxide produces methyl phenyl sulfoxide due to the protic solvent CH_3OH. Note that the authors drew the catalytic cycle of TEMPO backward. ARS-sensitized semiconductor photocatalysis has been deeply studied in the oxidation of sulfides.[17] The results showed that the solvent and light spectrum had significant influences on the selectivity and conversation, while the TEMPO derivatives had little influence (Scheme 6).

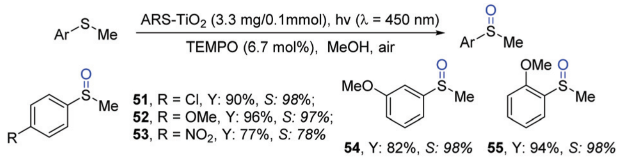
Last year, Han and co-workers prepared hollow anatase TiO_2 octahedrons which could be used in selective oxidation of organic sulfides.[18] The screening of light sources showed that blue light performed better than yellow light and green light. Under the irradiation of blue LEDs, dispersed ARS-TiO_2 (HTO-102 catalysts) showed general catalytic activation and high selectivity to various thioanisole derivatives. However, thioanisole derivatives containing a strong electron-withdrawing group (NO_2, **53**, 77%) react less efficiently than those containing an electron-donating group (OMe, **52**, 96%). The methoxy substitution position on the aromatic ring has little effect on the reaction (**52**, **54–55**). Later, dehydro-coupling of the thiols could be realized with cesium lead halide perovskite nanocrystals[19] and the Co–N–TiO_2 photocatalyst[20] to synthesize disulfides (Scheme 7).

2.3 Oxidation of α-heteroatom C–H bonds

The classical oxidation of C(sp^3)–H bonds adjacent to nitrogen is achieved using expensive Ir or Ru complexes.[21] Later, this



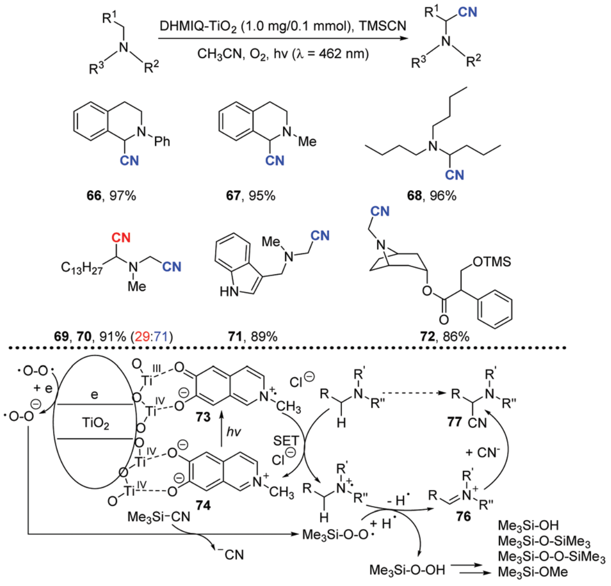
Scheme 6 The selective aerobic oxidation of sulfides with ARS-TiO_2.



Scheme 7 The selective aerobic oxidation of sulfides with ARS-TiO_2 octahedrons.

photocatalytic cross-dehydrogenative coupling reaction was realized with a heterogeneous TiO_2 photocatalyst.[22] A variety of functionalized substituted 2-phenyl-1,2,3,4-tetrahydroisoquinolines was obtained in high yields. After 5 cycles of the aza-Henry reaction, TiO_2 did not lose any reactivity or selectivity (Scheme 8).

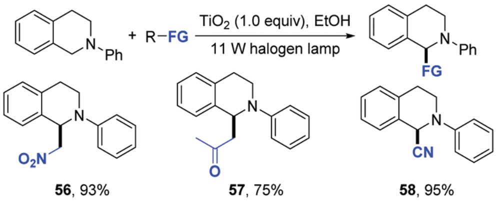
Recently, a nanocrystalline TiO_2-grafted ruthenium(II) polyazine complex was successfully synthesized and used in oxidative cyanation of tertiary amines to overcome the drawbacks of difficult recovery of Ru(II)polypyridine complexes.[23] Various substituted *N*,*N*-dimethylanilines are tolerated (**59–62**), as well as secondary aryl amines (**63**). However, benzylic amines (**64**) show low reactivity, while alkyl amines (**65**) are not compatible (Scheme 9).



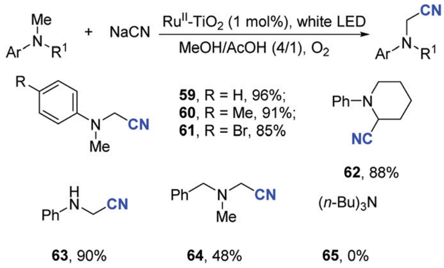
Scheme 10 The oxidative cyanation catalyzed by DHMIQ-sensitized TiO_2 NPs.

Opatz and Tremel developed a light-absorbing chromophore, 6,7-dihydroxy-2-methylisoquinolinium (DHMIQ), which was further used in the synthesis of DHMIQ-sensitized TiO_2 NPs (Scheme 10).[24] This new photocatalyst enables efficient oxidative cyanation of tertiary amines (**66–67**, **71**), especially tertiary alkyl amines (**68**). The reaction appears to favor primary C–H bonds (**69–71**). For atropine, cyanation could also occur (**72**). In the proposed mechanism, under irradiation, single electron transfer occurrs between the excited DHMIQ and tertiary amines, associated with injection of an electron into the TiO_2 conduction band. The $O_2^{\bullet-}$ radical anion generated from O_2 reacts with TMSCN to produce CN^-, which further attacks iminium ion **76** to deliver the final cyanation products.

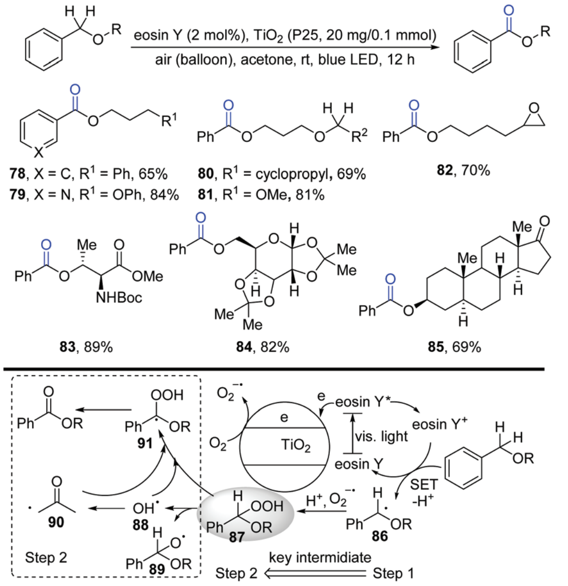
With the aid of dye-sensitized TiO_2, Cong and co-workers disclosed the aerobic photooxidation of benzyl ethers to benzoates (Scheme 11).[25] Aromatic and heteroaromatic benzylic C–H bonds could be efficiently oxidized to produce esters (**78–79**). Interestingly, electron-rich C–H bonds were also toler-



Scheme 8 Functionalization of tetrahydroisoquinolines catalyzed by TiO_2.



Scheme 9 Oxidative cyanation of tertiary amines with the Ru^{II}–TiO_2 polyazine complex.

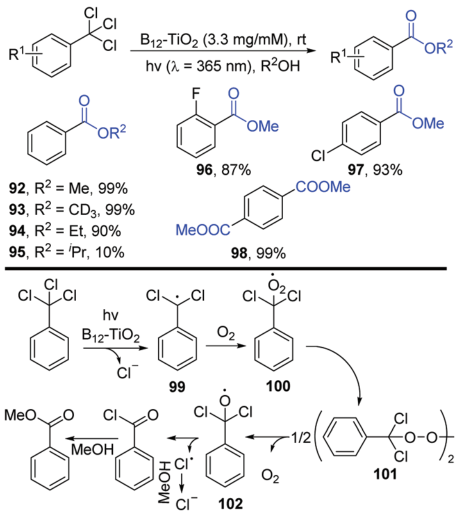


Scheme 11 Selective aerobic oxidation of benzyl ethers with eosin Y-TiO_2.

ated (**80–82**). Natural product-derived benzyl ethers could be transformed into the desired products, such as threonine, monosaccharide, and epiandrosterone (**83–85**). In addition, a peroxide intermediate **87** was obviously observed from the kinetic profiles and was successfully isolated in 47% yield after 1 h under the standard conditions. Following the general procedure, SET occurs from the substrate to the oxidized form eosin Y to generate benzylic radical **86**, which can react with superoxide radical to produce the key peroxide intermediate **87**. This is followed by homolysis of the labile O–O bond, by which two different radicals (**88**, **89**) are produced. Among these, hydroxyl radical can absorb an H atom from acetone, forming a new radical species (**90**). The two radical species (**88** and **89**) react with **87** to generate **91**, which can be transformed into the final ester.

2.4 Others

In 2015, a hybrid catalyst in which B_{12} was coordinated to the surface of TiO_2 was successfully used in catalytic dechlorination of trichlorinated organic compounds to produce esters.[26] The common primary alcohols could efficiently react with the dechlorination intermediate to afford the corresponding esters (**92–95**), while ^{i}PrOH with steric hindrance afforded **95** in low yield (10%). Halogen-substituted aryl trichlorides were also tolerated (**96–97**). However, the alkyl trichlorides showed lower reactivity. Interestingly, dimethyl acetal was obtained in 99% yield (**98**). In addition, when excess primary and secondary amines were added, the reaction could afford amides in high yields (79% to 95%). The dichloromethylbenzene radical (**99**) is produced from trichloromethylbenzene by the reduction of the Co^{I} species in B_{12}-TiO_2, which rapidly reacts with O_2 to form the peroxy radical. The benzoyl chloride is produced through disproportionation and dechlorination from **101**. In the presence of alcohols, the corresponding ester is finally formed (Scheme 12).

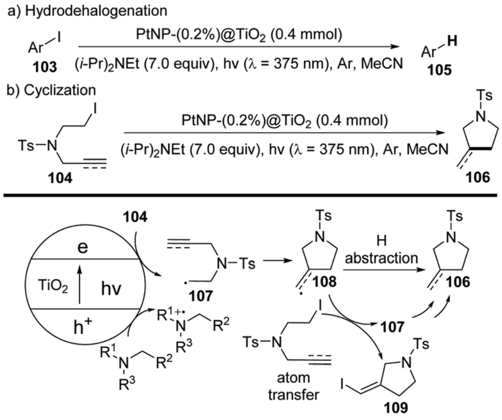


Scheme 12 Dechlorination of benzotrichlorides with B_{12}-TiO_2.

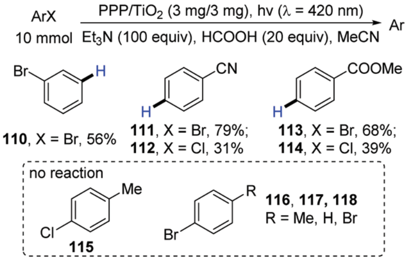
3. Reductive reactions

In 2014, platinum nanoparticles on titania (PtNP@TiO_2) were applied in photoredox reductive transformations using $^{i}Pr_2NEt$ as a sacrificial reagent.[27] Compared to TiO_2, this new photocatalyst could extend the absorption spectral width and was expected to decrease electron–hole pair recombination by increasing interfacial electron transfer, resulting in enhancement of the photocatalytic reactivity. After hydrodehalogenation of the aryl iodides, intramolecular cyclization also occurred. The proposed mechanism is shown in Scheme 13. When the reactant is aryl iodines **103**, the SET and HAT processes afford the reductive product **105**. For alkyl iodines, **104** undergoes a single reduction to produce alkyl radical **107**, followed by an intramolecular addition to obtain **108**. The intermediate **108** absorbs an H atom to afford the final cyclization product **106**. Later, CdS–TiO_2 composite nanosheets (CdS–TiO_2–NS) were prepared from TiO_2 nanosheets and CdS nanocrystals. When used in the reduction of nitroaromatics, the CdS–TiO_2–NS-60 composite showed significantly higher activity than the TiO_2 nanosheets.[28] Recently, the less expensive and toxic metal Co was used as a co-catalyst. The composite of CoOx supported on TiO_2 nanosheets showed effective reductive ability for diverse nitroarenes and nitropyridines in the presence of hydrazine monohydrate as a reductant under visible light irradiation.[29] It is worth noting that the chemoselective reduction of nitro groups was achieved by using 1,5-dimethyl-4-nitro-2-phenyl-1*H*-pyrazole-3(2*H*)-one as a reactant.

Although polymer poly(pphenylene) (PPP) can be used as a photoredox catalyst, it shows low catalytic activity for organic reactions and requires several days to complete the transformations.[30] Conjugated polymer and TiO_2 nanocomposites exhibit higher photocatalytic degradation of phenol.[31] Inspired by this work, Nazer and McCulla hypothesized that combined PPP and TiO_2 photocatalysts could efficiently catalyze dehalogenation of aryl halides.[32] 1,3-Dibromobenzene (**110**), 4-halogen-substituted benzonitrilse (**111–112**), and benzoates (**113–114**) could undergo dehalogenation, while low yields of aryl chlorides (**112**, **114**) (31% and 39%) were obtained. The



Scheme 13 Hydrodehalogenation with PtNP@TiO_2.



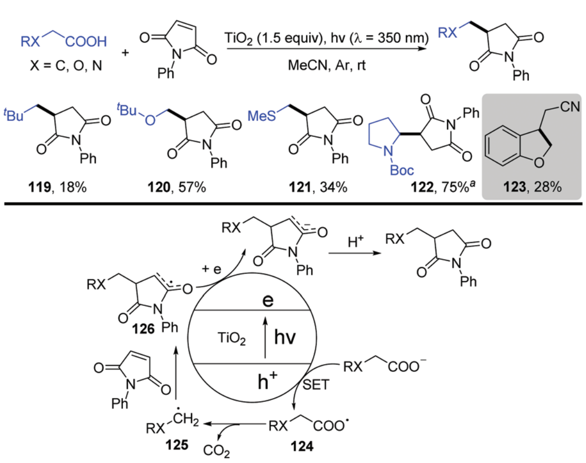
Scheme 14 Hydrodehalogenation with PPP-TiO_2.

reduction potential of these aryl halides is more positive than −1.5 V *vs.* Ag/AgBr. When the reduction potential is more negative than −1.5 V, aryl halides, even bromobenzene, are not tolerated in the photocatalytic dehalogenation (**115–118**). These results may be related to the conduction band potential of PPP (−1.7 V *vs.* Ag/AgBr) (Scheme 14).

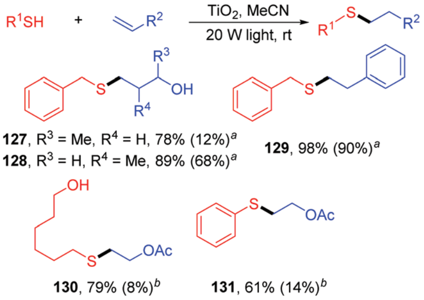
4. Addition reactions

Carboxylic acids are prevalent in nature. Walton disclosed a decarboxylative addition and cyclization catalyzed by TiO_2.[33] Generally, primary alkyl radicals stabilized by α-heteroatoms showed better reactivity (**119–123**). Similarly to the homogeneous decarboxylative process,[34] carboxylate is oxidized by TiO_2, followed by decarboxylation to generate alkyl radical **125**. The radical intermediate **125** adds rapidly to the electron-deficient double bonds to produce **126**, which undergoes a SET process and protonation to generate the final adducts. When a double bond and a carboxyl group are present in one molecule, intermolecular radical addition–cyclization occurs (**123**) (Scheme 15).

Based on previous work,[35] Greaney proposed that binding thiols to the surface of TiO_2 could enable electron transfer under the irradiation of visible light.[36] Deprotonation of the thiyl radical cation can lead to a thiyl radical, which subsequently undergoes addition to an alkene; absorption of an H atom from the thiol produces the desired product. As shown in Scheme 16, 1 equiv. TiO_2 could promote the radical addition of phenylmethanethiol to alkenes (**127**), while TiO_2 shows little effect on alkenes substituted with methyl at the 3-position (**128**) or styrenes (**129**). Both alkyl thiols and thiophenols could undergo radical addition of alkenes (**130–131**). In the presence of O_2, disulfides were obtained.[37]



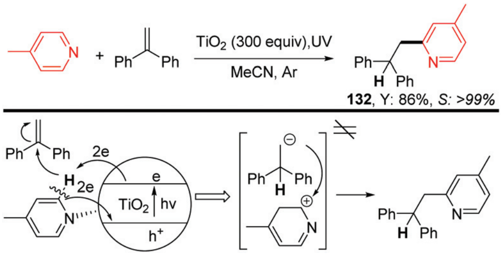
Scheme 15 TiO_2-promoted alkylations of *N*-phenylmaleimide with carboxylic acids. ^{a} 1 : 1 mixture of two diastereoisomers.



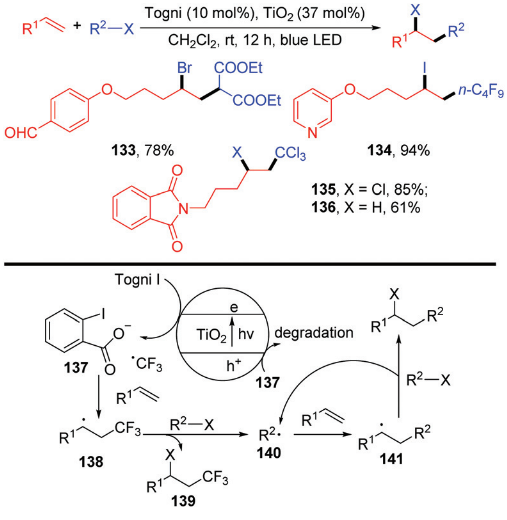
Scheme 16 Thiol–ene reaction catalyzed by TiO_2. ^{a} TiO_2 (1.0 equiv.), 16 h. ^{b} TiO_2 (0.1 equiv.), 40 h. Note: numbers in parentheses are the yield without TiO_2.

In addition to the typical radical addition, Chen and Zhao disclosed ionic addition through a two-electron transfer pathway *via* TiO_2 photocatalysis.[38] Under the optimal reaction conditions, the pyridine C–H bond was activated, enabling addition to ethene-1,1-diyldibenzene to afford the desired product (**132**) in excellent yield (90%). The yield did not decrease in the presence of the radical-traping reagent TEMPO. As shown in Scheme 17, two-electron oxidation occurs to generate the cation, which finally leads to product **132** *via* nucleophilic attack.

For atom-transfer radical addition (ATRA),[39] Cao and coworkers used TiO_2 to catalyse alkyl halides to finish it under mild conditions.[40] Under irradiation, unactivated terminal alkenes were successfully applied in ATRA using common diethyl bromomalonate (**133**) and perfluorobutyl iodide (**134**) as atom-transfer reagents. More importantly, challenging chlorides are also compatible (**135–136**). In the reaction, a catalytic amount of Togni I acts as the promoter, releasing benzoate anion **137** and trifluoromethyl radical. Initial radical addition affords intermediate **138**, which reacts with the atom-transfer reagent to generate the key radical **140** with byproduct



Scheme 17 TiO_2 photocatalytic addition of 4-picoline to 1,1-diphenylethylene.



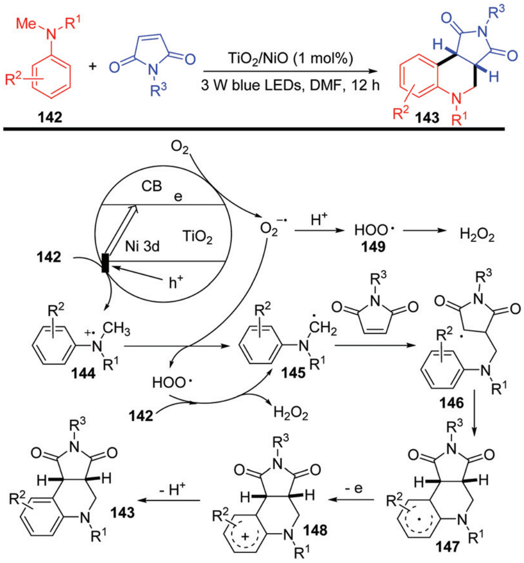
Scheme 18 Atom-transfer radical addition with TiO_2.

139. The final radical addition and atom transfer afford the corresponding product, and a radical chain transfer cycle completes the reaction (Scheme 18).

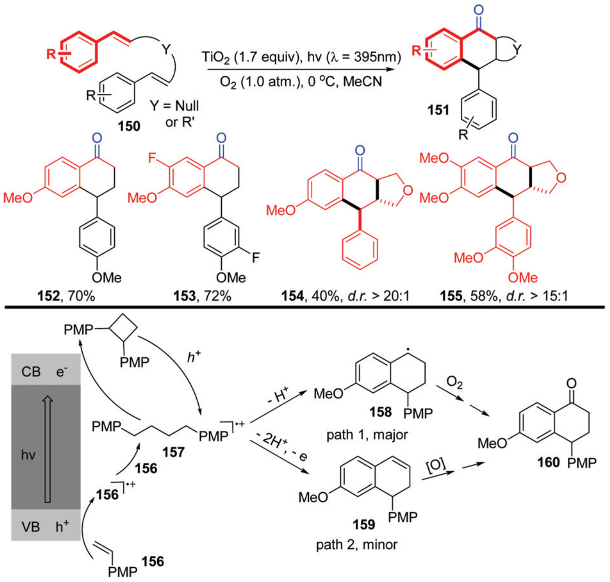
5. Cyclo(addition) reactions

In 2015, novel titanium dioxides surface-modified with highly dispersed NiO particles showed decreased hole–electron pair recombination, enhancing their visible light photocatalytic activity.[41] This heterogeneous catalyst provides access to tetrahydroquinolines (**143**). Usually, tertiary anilines are oxidized by the excited semiconductor catalyst to afford the amine cation radical **144**, which rapidly undergoes proton transfer to form the α-aminoalkyl radical **145**. **145** undergoes addition to the maleimide to afford intermediate **146**; this is followed by cycloaddition, electron transfer and subsequent deprotonation to provide the final product tetrahydroquinolines (**143**). In addition, HAT from **147** to form a hydroperoxide radical can lead to **143**. A similar reaction was achieved using Alizarin red S–TiO_2 (Scheme 19).[42]

In 2016, Wang and co-workers disclosed a TiO_2-catalyzed tandem reaction to achieve efficient oxidative cyclization for the syntheses of aryltetralones.[43] Intermolecular (**152–153**) and intramolecular (**154–155**) cycloaddition reactions were successfully achieved. When conducted under Ar atmosphere, the reaction produced the [2 + 2] cycloadduct **160**, but in low yield. ^{18}O-label experiments ($Ti^{18}O_2$, $H_2{}^{18}O$, $^{18}O_2$, respectively) suggested that the oxygen atom in the aryltetralones originates from O_2. Firstly, a dimeric radical cation **157** is formed by the radical tandem reaction. In the presence of Ar, [2 + 2] cycloadducts are obtained. Then, the key radical cation **157** may follow two possible pathways. Deproton is the major pathway; it affords cyclization radical intermediate **158**. Cyclenes **159** can be obtained by pathway 2. The two species are further oxidized to deliver the final aryltetralones (Scheme 20).



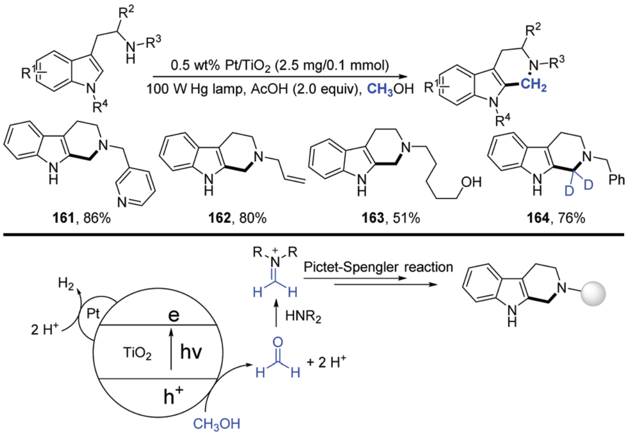
Scheme 19 Cycloadditions of tertiary anilines and maleimides with TiO_2/NiO.



Scheme 20 Oxidative cycloadditions with TiO_2.

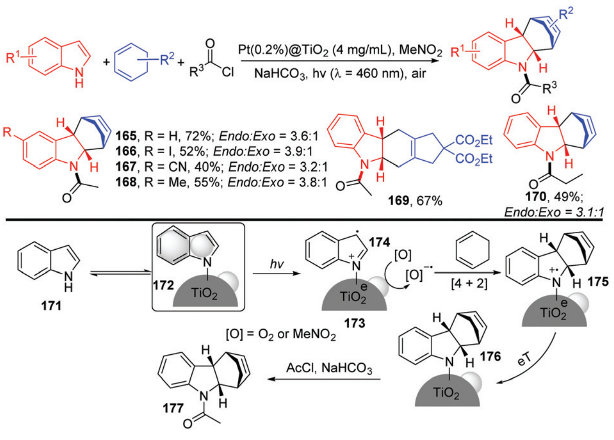
In consideration of the proton-reducing ability of Pt, Pt-doped TiO_2 particles were synthesized for photocatalytic dehydrogenative Pictet–Spengler cyclizations.[44] Various groups were found to be tolerated, including alkenes, unprotected alcohols and pyridine substituents (**161–163**). When using CD_3OH, the deuteration-labeled cyclization product was afforded in high yield (**164**). The key reaction step is MeOH dehydrogenation; it affords formaldehyde equivalents, which subsequently react with amines to produce the final products through Pictet–Spengler cyclization reactions (Scheme 21).

In 2017, Yoon found that the absorption spectrum of TiO_2 showed a significant red shift in the presence of an indole

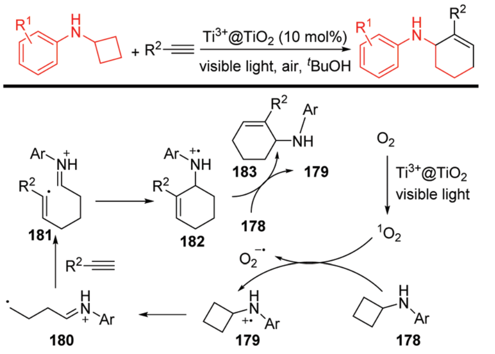


Scheme 21 Dehydrogenative Pictet–Spengler cyclizations with Pt/TiO$_2$.

(Scheme 22).[45] Therefore, Diels–Alder cycloaddition between indoles and 1,3-cyclohexadiene was disclosed, mediated by TiO$_2$ particles under blue LED irradiation. Soon, the Pt(0.2%)@TiO$_2$ catalyst was applied in enhanced photooxidative Diels–Alder reactions of indoles with electron-rich dienes.[46] The reaction exhibited a broad functional group tolerance (**165–168**). Substituted dienes were also compatible (**169**). Increasing the bulk of the acetyl chloride led to decreased yield (**170**). Firstly, the complex **172** is produced when the indole is absorbed on the surface of TiO$_2$. Then, the excited **172** injects an electron into the CB of TiO$_2$ with the aid of an external oxidant to prevent back-electron transfer. Eventually, the generated indole radical cation **174** undergoes a [4 + 2] cycloaddition with 1,3 CHD, followed by eT from the CB of TiO$_2$ and *in situ* acylation to avoid overoxidation, affording the final acylated cycloadducts **177**.



Scheme 22 Diels–Alder cycloaddition catalyzed by Pt(0.2%)@TiO$_2$.

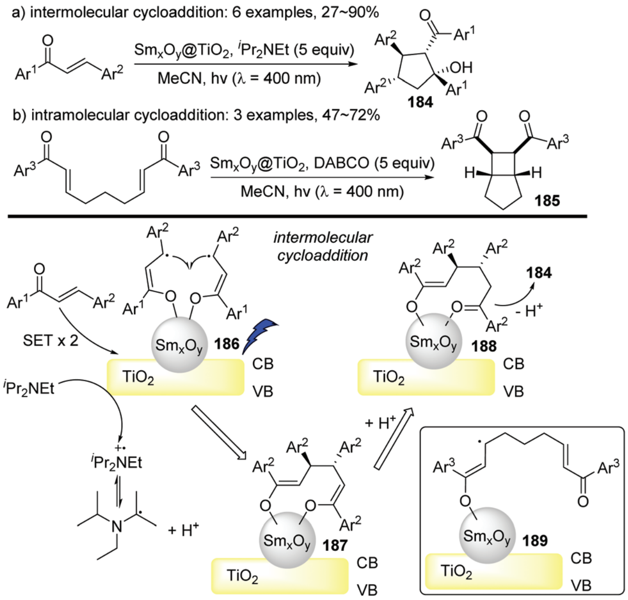


Scheme 23 The [4 + 2] annulation catalyzed by self-doped Ti^{3+}@TiO$_2$.

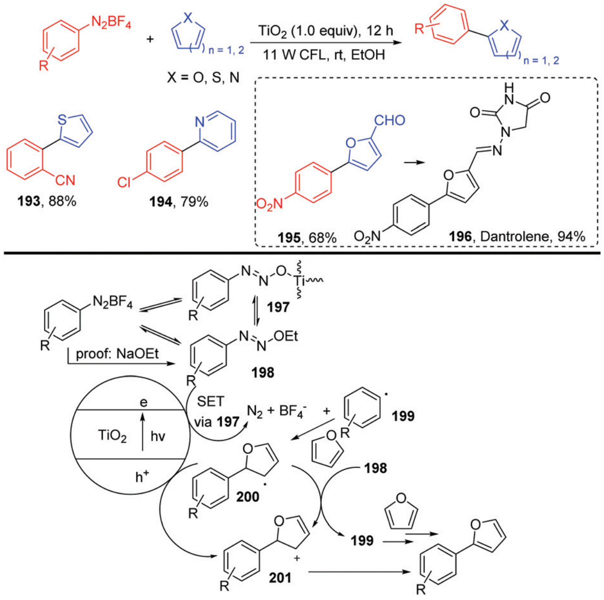
As an alternative method to narrow the band gap of TiO$_2$, self-doped Ti^{3+}@TiO$_2$ was developed.[47] Based on their previous success, Feng's group continued to investigate its use to catalyze organic reactions. After optimization of the reaction, [4 + 2] annulation between cyclobutylanilines and alkynes was realized by self-doped Ti^{3+}@TiO$_2$ in ^{t}BuOH. Surprisingly, Ti^{3+}@TiO$_2$ retained high photocatalytic activity after five cycles. Singlet oxygen, generated by energy transfer in the presence of a photosensitizer, is the active species for oxidation of amines **178**. The amine radical **179** undergoes a ring-opening process to generate radical intermediate **180**, followed by intermolecular addition to the alkyne. The intermediate **182** is obtained. The authors proposed a chain process. Finally, SET occurred between **182** and **178** to deliver the cyclohexenyl ring **183** and complete the reaction (Scheme 23).

In homogeneous reactions, cooperative photoredox-Lewis acid dual catalysis has made significant progress;[48] meanwhile, a few examples of heterogeneous reactions have been reported. Hence, Scaiano disclosed heterogeneous dual photoredox-Lewis acid catalysis with samarium oxide NPs (SmxOy@TiO$_2$).[49] When intermolecular cyclization occurred, cyclopentanol derivatives with five-membered rings were formed in moderate to high yields (**184**, 27% to 90%), while unmodified TiO$_2$ afforded relatively low yields. By simply replacing ^{i}Pr$_2$NEt with DABCO, intramolecular [2 + 2] cycloaddition could be achieved (**185**). Taking intermolecular cyclization as an example, the mechanism starts with the coordination of two molecules of the substrates to the photocatalysts **186**. Then, two SET events occur, followed by radical–radical coupling to form a C–C bond. **187** undergoes protonation followed by aldol addition to construct the final cyclopentanols. For intramolecular cycloaddtion, the key intermediate **189**, generated from the LA-activated substrate through SET, undergoes intramolecular Michael addition to form a five-membered ring, followed by cyclobutanation and loss of an electron to construct the final cycloadduct **185** (Scheme 24).

Last year, on the basis of the use of LiClO$_4$/CH$_3$NO$_2$ electrolyte solution[50] and the "electron relay" mechanism,[51] Okada developed an aromatic "redox tag"-guided intermolecular formal [2 + 2] cycloaddition with excess TiO$_2$.[52] After fast anchoring of the enol ether onto the TiO$_2$ surface, SET occurs to produce the radical cation, which is trapped by 1-hexene to generate the radical cation **190**. This process is facilitated by the remarkable Lewis acidity of the LiClO$_4$/CH$_3$NO$_2$ electrolyte solution. The intermediate **190** undergoes two reduction events, namely redox tag-assisted intramolecular SET and



Scheme 24 Dual photoredox-Lewis acid catalysis with SmxOy@TiO$_2$.



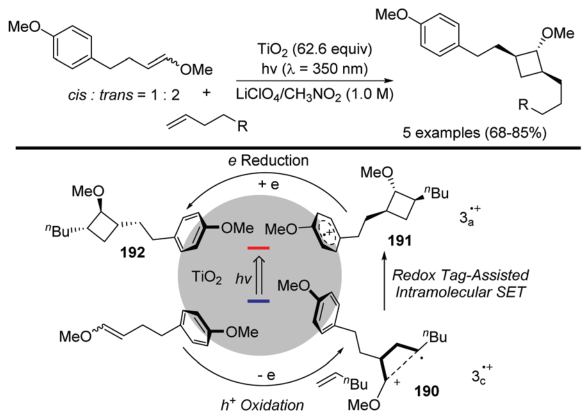
Scheme 26 C–H arylation of heteroarenes with TiO$_2$.

reduction of the excited electron on the surface of TiO$_2$. Finally, [2 + 2] cycloaddition products are formed. Later, a similar reaction system was applied in radical cation Diels–Alder reactions by the same group (Scheme 25).[53]

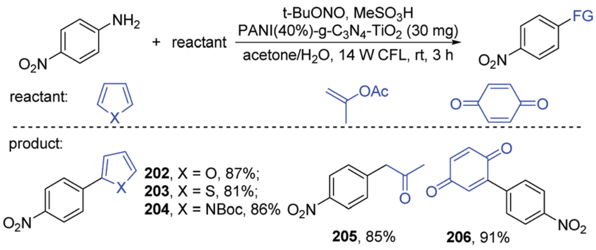
6. Cross-coupling reactions

Despite the significant progress in photocatalytic C–H arylation with diazonium salts,[54] it is still highly desirable to develop a practical method with an easily accessible, recyclable catalyst. Rueping first disclosed direct arylation of heteroaromatics catalyzed by a heterogeneous TiO$_2$ catalyst using aryl diazonium salts.[55] The arylation of furan and thiophene, as well as electron-poor pyridine, was successfully developed, and the corresponding aryl products were obtained in high yields (**193–195**). The aryl product **195** could be transformed into the muscle relaxant Dantrolene in 94% yield (**196**). In addition, the collected photocatalyst showed recyclability. The mechanism starts with a transetherification that affords TiO$_2$-azoether **197**, which can absorb visible light. Under irradiation, SET occurs to afford the aryl radical. The following radical addition and oxidation affords the intermediate cation **201**. Finally, the rearomatization of **201** generates the aryl product. Two years later, the same reaction was successfully performed in a microstructured falling film reactor with continuous-flow C–H arylation by the same group (Scheme 26).[56]

Recently, Wang synthesized polyaniline-g-C$_3$N$_4$–TiO$_2$ composite and used it in the synthesis of α-chloro aryl ketones.[57] In the reaction, the phenylacetylene was used as an aryl radical acceptor. Then, the radical adduct intermediate underwent oxidation by molecular oxygen, capturing a proton, followed by attack of Cl$^-$ to deliver the final α-chloro aryl ketones. Later, the same PANI–g-C$_3$N$_4$–TiO$_2$ composite was used in a greener approach for C–H arylation in aqueous medium (Scheme 27).[58] Anilines were used as raw materials, and aryl diazonium salts *in situ* formed in the presence of *t*-BuONO and MeSO$_3$H. Diverse heteroarenes containing O, S, and N atoms were compatible in the reaction (**202–204**). In addition,



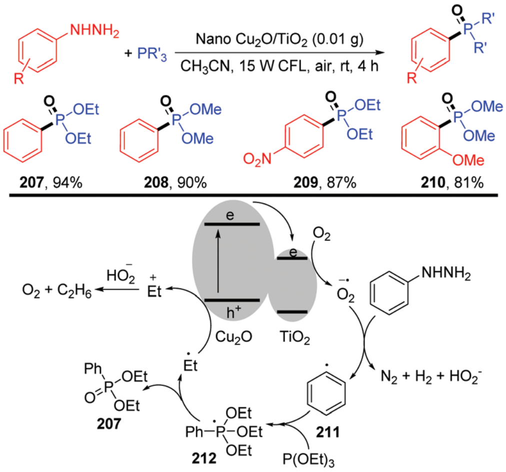
Scheme 25 [2 + 2] cycloadditions promoted by LiClO$_4$/CH$_3$NO$_2$ with TiO$_2$.



Scheme 27 C–H arylation of heteroarenes with the g-C$_3$N$_4$–TiO$_2$ composite.

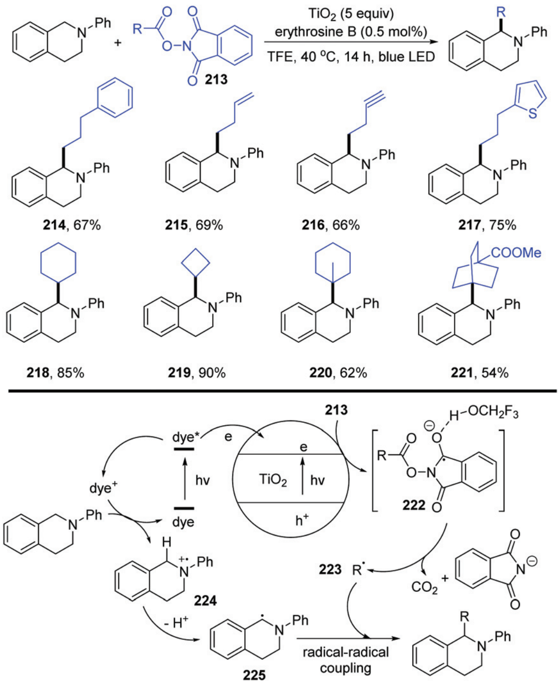
α-aryl ketone motifs (**205**) and arylated benzoquinones (**206**) were formed from prop-1-en-2-yl acetate and benzoquinone.

In addition to aryl diazonium salts, phenylhydrazine can serve as a precursor of aryl radicals in aerobic conditions.[59] With the aid of Cu_2O, which is able to absorb visible light, synthesized Cu_2O/TiO_2 nanoparticles were used in the formation of arylphosphonates. Alkyl-phosphonates, such as $P(OMe)_3$ and $P(OEt)_3$, could be used as phosphonylation reagents to afford the corresponding arylphosphonates (**207–208**) in excellent yield (90% to 94%). Electron-donating groups (OMe, **210**) and electron-withdrawing groups (NO_2, **209**) were also tolerated. Under visible irradiation, the excited Cu_2O transfers an electron to TiO_2. The electron is absorbed by O_2 to generate the superoxide radical anion, which subsequently reacts with phenylhydrazine to produce aryl radical **211**. The unstable intermediate **212** is formed in the presence of $P(OEt)_3$. After releasing ethyl radical, the arylphosphonates are obtained (Scheme 28).



Scheme 28 C–P bond formation of arylhydrazine and trialkylphosphite using the nano Cu_2O/TiO_2 photocatalyst.

N-Hydroxyphthalimide esters have been widely used as radical precursors.[60] In heterogeneous photocatalysis, *N*-hydroxyphthalimide esters can be applied in decarboxylative alkylation of tetrahydroisoquinoline derivatives.[61] Surprisingly, the present reaction can tolerate unactivated primary (**214–217**), secondary (**218–219**), and tertiary (**220–221**) alkyl-substituted *N*-hydroxyphthalimide esters. The mechanism starts with two independent SET events. The solvent TFE can stabilize the radical intermediate **222** *via* hydrogen bonding. After hemolytic cleavage of the N–O bond, alkyl radical **223** is obtained. Subsequent radical–radical coupling affords the final product (Scheme 29).



Scheme 29 Decarboxylative alkylation of C–H bonds catalyzed by erythrosine B-sensitized TiO_2.

7. Conclusions

In recent years, a large number of TiO_2-based materials have been synthesized, and increasing attention has been paid to their photocatalytic application in organic transformation. In this review, the recent reports of photocatalytic transformation catalyzed by TiO_2 and modified TiO_2 have been mainly summarized. Due to the large band gap and lack of absorption of visible light of unmodified TiO_2, modified TiO_2 catalysts have broader and more effective synthetic applications.

Despite significant progress, there are still considerable opportunities and challenges in this field. New co-catalysts can be selected to improve the photocatalysis of TiO_2 for organic reactions. Meanwhile, diverse modified TiO_2 materials synthesized by inorganic chemists may have unique photocatalytic character for special and challenging organic reactions. Another opportunity is the development of novel reactions. In addition, continuous flow chemistry will provide a good opportunity for newly designed reactors. Given the advantages of heterogeneous photocatalysis in organic chemistry,[62] we believe that this timely review will arouse considerable enthusiasm in the near future.

Abbreviation

C	Conversion
Y	Yield
S	Selectivity
MOFs	Metal–organic frameworks
AR	Alizarin Red
ARS	Alizarin Red S
BTF	Benzotrifluoride
PW_{12}	$PW_{12}O_{40}{}^{3-}$
TH	Thionine

DHMIQ	6,7-Dihydroxy-2-methylisoquinolinium
TEA	Triethylamine
CB	Conduction band
VB	Valence band
DABCO	Triethylene diamine
TFE	2,2,2-Trifluoroethanol
PPP	Poly(pphenylene)
LA	Lewis acid
1,3-CHD	1,3-Cylohexadiene

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Mr Xu was supported by the Scientific Research Foundation of Graduate School of Nanjing University (No. 2018CL05). We thank Dr Weipeng Li of Nanjing University for proof-reading.

Notes and references

1 R. D. Cortright, R. R. Davda and J. A. Dumesic, *Nature*, 2002, **418**, 964.

2 (*a*) A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253; (*b*) T. J. Meyer, *Acc. Chem. Res.*, 2002, **22**, 163.

3 (*a*) K. Kalyanasundaram, *Coord. Chem. Rev.*, 1998, **177**, 347; (*b*) X. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746.

4 (*a*) K. L. Skubi, T. R. Blum and T. P. Yoon, *Chem. Rev.*, 2016, **116**, 10035; (*b*) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075; (*c*) C. K. Prier, D. A. Rankic and D. W. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (*d*) M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898; (*e*) L. Marzo, S. K. Pagire, O. Reiser and B. Konig, *Angew. Chem., Int. Ed.*, 2018, **57**, 10034; (*f*) I. K. Sideri, E. Voutyritsa and C. G. Kokotos, *Org. Biomol. Chem.*, 2018, **16**, 4596.

5 (*a*) J. Kou, C. Lu, J. Wang, Y. Chen, Z. Xu and R. S. Varma, *Chem. Rev.*, 2017, **117**, 1445; (*b*) L. Chen, J. Tang, L.-N. Song, P. Chen, J. He, C.-T. Au and S.-F. Yin, *Appl. Catal., B*, 2019, **242**, 379.

6 (*a*) X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891; (*b*) Y. Wu, M. Xing, B. Tian, J. Zhang and F. Chen, *Chem. Eng. J.*, 2010, **162**, 710; (*c*) Y. Zheng, Z. Pan and X. Wang, *Chin. J. Catal.*, 2013, **34**, 524; (*d*) H. Xu, S. Ouyang, L. Liu, P. Reunchan, N. Umezawa and J. Ye, *J. Mater. Chem. A*, 2014, **2**, 12642.

7 (*a*) V. Etacheri, C. Di Valentin, J. Schneider, D. Bahnemann and S. C. Pillai, *J. Photochem. Photobiol., C*, 2015, **25**, 1; (*b*) A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol., C*, 2000, **1**, 1; (*c*) K. Nakata and A. Fujishima, *J. Photochem. Photobiol., C*, 2012, **13**, 169; (*d*) Z. Xiong, Z. Lei, Y. Li, L. Dong, Y. Zhao and J. Zhang, *J. Photochem. Photobiol., C*, 2018, **36**, 24; (*e*) L. E. Oi, M.-Y. Choo, H. V. Lee, H. C. Ong, S. B. A. Hamid and J. C. Juan, *RSC Adv.*, 2016, **6**, 108741; (*f*) N. Hoffmann, *Aust. J. Chem.*, 2015, **68**, 1621.

8 Y. Shiraishi and T. Hirai, *J. Photochem. Photobiol., C*, 2008, **9**, 157.

9 J. Z. Bloh and R. Marschall, *Eur. J. Org. Chem.*, 2017, 2085.

10 M. Zhang, C. Chen, W. Ma and J. Zhao, *Angew. Chem., Int. Ed.*, 2008, **47**, 9730.

11 Q. Wang, M. Zhang, C. Chen, W. Ma and J. Zhao, *Angew. Chem., Int. Ed.*, 2010, **49**, 7976.

12 X. Yang, H. Zhao, J. Feng, Y. Chen, S. Gao and R. Cao, *J. Catal.*, 2017, **351**, 59.

13 X. Li, J.-L. Shi, H. Hao and X. Lang, *Appl. Catal., B*, 2018, **232**, 260.

14 X. Lang, W. R. Leow, J. Zhao and X. Chen, *Chem. Sci.*, 2015, **6**, 1075.

15 X. Lang, W. Hao, W. R. Leow, S. Li, J. Zhao and X. Chen, *Chem. Sci.*, 2015, **6**, 5000.

16 X. Lang, J. Zhao and X. Chen, *Angew. Chem., Int. Ed.*, 2016, **55**, 4697.

17 H. Hao, Z. Wang, J.-L. Shi, X. Li and X. Lang, *ChemCatChem*, 2018, **10**, 4545.

18 F. Wang, L. Sun, Y. Li, W. Zhan, X. Wang and X. Han, *Inorg. Chem.*, 2018, **57**, 4550.

19 W.-B. Wu, Y.-C. Wong, Z.-K. Tan and J. Wu, *Catal. Sci. Technol.*, 2018, **8**, 4257.

20 M. Zou, L. Feng, T. Thomas and M. Yang, *Catal. Sci. Technol.*, 2017, **7**, 4182.

21 (*a*) A. G. Condie, J. C. Gonzalez-Gomez and C. R. Stephenson, *J. Am. Chem. Soc.*, 2010, **132**, 1464; (*b*) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny and D. C. Fabry, *Chem. Commun.*, 2011, **47**, 2360; (*c*) M. Rueping, S. Zhu and R. M. Koenigs, *Chem. Commun.*, 2011, **47**, 12709.

22 M. Rueping, J. Zoller, D. C. Fabry, K. Poscharny, R. M. Koenigs, T. E. Weirich and J. Mayer, *Chem. – Eur. J.*, 2012, **18**, 3478.

23 P. Kumar, S. Varma and S. L. Jain, *J. Mater. Chem. A*, 2014, **2**, 4514.

24 A. M. Nauth, E. Schechtel, R. Doren, W. Tremel and T. Opatz, *J. Am. Chem. Soc.*, 2018, **140**, 14169.

25 L. Ren, M.-M. Yang, C.-H. Tung, L.-Z. Wu and H. Cong, *ACS Catal.*, 2017, **7**, 8134.

26 H. Shimakoshi and Y. Hisaeda, *Angew. Chem., Int. Ed.*, 2015, **54**, 15439.

27 C. D. McTiernan, S. P. Pitre, H. Ismaili and J. C. Scaiano, *Adv. Synth. Catal.*, 2014, **356**, 2819.

28 X. Pan and Y.-J. Xu, *J. Phys. Chem. C*, 2015, **119**, 7184.

29 S. R. Amanchi, K. V. Ashok Kumar, B. Lakshminarayana, G. Satyanarayana and C. Subrahmanyam, *New J. Chem.*, 2019, **43**, 748.

30 W. D. Rouch, M. Zhang and R. D. McCulla, *Tetrahedron Lett.*, 2012, **53**, 4942.

31 X. Li, D. Wang, G. Cheng, Q. Luo, J. An and Y. Wang, *Appl. Catal., B*, 2008, **81**, 267.

32 J. T. Petroff Ii, A. H. Nguyen, A. J. Porter, F. D. Morales, M. P. Kennedy, D. Weinstein, H. E. Nazer and R. D. McCulla, *J. Photochem. Photobiol., A*, 2017, **335**, 149.

33 D. W. Manley, R. T. McBurney, P. Miller, J. C. Walton, A. Mills and C. O'Rourke, *J. Org. Chem.*, 2014, **79**, 1386.

34 (*a*) C. Shu, R. S. Mega, B. J. Andreassen, A. Noble and V. K. Aggarwal, *Angew. Chem., Int. Ed.*, 2018, **57**, 15430; (*b*) Q. Q. Zhou, W. Guo, W. Ding, X. Wu, X. Chen, L. Q. Lu and W. J. Xiao, *Angew. Chem., Int. Ed.*, 2015, **54**, 11196; (*c*) S. Ventre, F. R. Petronijevic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2015, **137**, 5654.

35 C. Vila and M. Rueping, *Green Chem.*, 2013, **15**, 2056.

36 V. T. Bhat, P. A. Duspara, S. Seo, N. S. B. Abu Bakar and M. F. Greaney, *Chem. Commun.*, 2015, **51**, 4383.

37 C. Bottecchia, N. Erdmann, P. M. Tijssen, L. G. Milroy, L. Brunsveld, V. Hessel and T. Noel, *ChemSusChem*, 2016, **9**, 1781.

38 D. Ma, Y. Yan, H. Ji, C. Chen and J. Zhao, *Chem. Commun.*, 2015, **51**, 17451.

39 (*a*) D. P. Curran, M. H. Chen, E. Spletzer, C. M. Seong and C. T. Chang, *J. Am. Chem. Soc.*, 1989, **111**, 8872; (*b*) H. Yorimitsu, T. Nakamura, H. Shinokubo, K. Oshima, K. Omoto and H. Fujimoto, *J. Am. Chem. Soc.*, 2000, **122**, 11041.

40 L. L. Mao and H. Cong, *ChemSusChem*, 2017, **10**, 4461.

41 J. Tang, G. Grampp, Y. Liu, B. X. Wang, F. F. Tao, L. J. Wang, X. Z. Liang, H. Q. Xiao and Y. M. Shen, *J. Org. Chem.*, 2015, **80**, 2724.

42 M. Hosseini-Sarvari, M. Koohgard, S. Firoozi, A. Mohajeri and H. Tavakolian, *New J. Chem.*, 2018, **42**, 6880.

43 Y. Liu, M. Zhang, C.-H. Tung and Y. Wang, *ACS Catal.*, 2016, **6**, 8389.

44 C. M. Adolph, J. Werth, R. Selvaraj, E. C. Wegener and C. Uyeda, *J. Org. Chem.*, 2017, **82**, 5959.

45 S. P. Pitre, T. P. Yoon and J. C. Scaiano, *Chem. Commun.*, 2017, **53**, 4335.

46 S. P. Pitre, J. C. Scaiano and T. P. Yoon, *ACS Catal.*, 2017, **7**, 6440.

47 (*a*) F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt and P. Feng, *J. Am. Chem. Soc.*, 2010, **132**, 11856; (*b*) F. Zuo, K. Bozhilov, R. J. Dillon, L. Wang, P. Smith, X. Zhao, C. Bardeen and P. Feng, *Angew. Chem., Int. Ed.*, 2012, **51**, 6223.

48 T. P. Yoon, *Acc. Chem. Res.*, 2016, **49**, 2307.

49 G. K. Hodgson and J. C. Scaiano, *ACS Catal.*, 2018, **8**, 2914.

50 (*a*) S. Kim, T. Shoji, Y. Kitano and K. Chiba, *Chem. Commun.*, 2013, **49**, 6525; (*b*) T. Shoji, S. Kim, K. Yamamoto, T. Kawai, Y. Okada and K. Chiba, *Org. Lett.*, 2014, **16**, 6404.

51 (*a*) J. J. Murphy, D. Bastida, S. Paria, M. Fagnoni and P. Melchiorre, *Nature*, 2016, **532**, 218; (*b*) A. Bahamonde, J. J. Murphy, M. Savarese, É. Brémond, A. Cavalli and P. Melchiorre, *J. Am. Chem. Soc.*, 2017, **139**, 4559.

52 Y. Okada, N. Maeta, K. Nakayama and H. Kamiya, *J. Org. Chem.*, 2018, **83**, 4948.

53 K. Nakayama, N. Maeta, G. Horiguchi, H. Kamiya and Y. Okada, *Org. Lett.*, 2019, **21**, 2246.

54 (*a*) M. R. Heinrich, *Chem. – Eur. J.*, 2009, **15**, 820; (*b*) D. P. Hari, P. Schroll and B. Konig, *J. Am. Chem. Soc.*, 2012, **134**, 2958; (*c*) F. Mo, G. Dong, Y. Zhang and J. Wang, *Org. Biomol. Chem.*, 2013, **11**, 1582.

55 J. Zoller, D. C. Fabry and M. Rueping, *ACS Catal.*, 2015, **5**, 3900.

56 D. C. Fabry, Y. A. Ho, R. Zapf, W. Tremel, M. Panthöfer, M. Rueping and T. H. Rehm, *Green Chem.*, 2017, **19**, 1911.

57 W. Liu, C. Wang and L. Wang, *Ind. Eng. Chem. Res.*, 2017, **56**, 6114.

58 L. Wang, J. Shen, S. Yang, W. Liu, Q. Chen and M. He, *Green Chem.*, 2018, **20**, 1290.

59 M. Hosseini-Sarvari, F. Jafari, A. Mohajeri and N. Hassani, *Catal. Sci. Technol.*, 2018, **8**, 4044.

60 (*a*) K. Okada, K. Okamoto and M. Oda, *J. Am. Chem. Soc.*, 1988, **110**, 8736; (*b*) K. Okada, K. Okamoto, N. Morita, K. Okubo and M. Oda, *J. Am. Chem. Soc.*, 1991, **113**, 9401; (*c*) L. Candish, M. Teders and F. Glorius, *J. Am. Chem. Soc.*, 2017, **139**, 7440; (*d*) J. T. Edwards, R. R. Merchant, K. S. McClymont, K. W. Knouse, T. Qin, L. R. Malins, B. Vokits, S. A. Shaw, D. H. Bao, F. L. Wei, T. Zhou, M. D. Eastgate and P. S. Baran, *Nature*, 2017, **545**, 213; (*e*) A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers and V. K. Aggarwal, *Science*, 2017, **357**, 283; (*f*) D. Wang, N. Zhu, P. Chen, Z. Lin and G. Liu, *J. Am. Chem. Soc.*, 2017, **139**, 15632; (*g*) W. Zhao, R. P. Wurz, J. C. Peters and G. C. Fu, *J. Am. Chem. Soc.*, 2017, **139**, 12153.

61 L. Ren and H. Cong, *Org. Lett.*, 2018, **20**, 3225.

62 I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti and B. Konig, *Science*, 2019, **365**, 360.