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The Application of Heterogeneous Visible Light Photocatalyst in Organic Synthesis

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The advantage of visible-light photocatalysis lies in its use of clean, renewable, cheap visible light as a driving force. Recently heterogeneous visible light photocatalysts have drawn much attention due to their nature of easy recycling and simple chemical work-up. Immense effort has been devoted to the application of solar energy in the field of energy regeneration such as hydrogen production and reduction of carbon dioxide. Recently the solar energy also has captured much attention in organic synthesis due to its unique advantages. This paper will review the state-of-the-art progresses in the application of heterogeneous visible-light photocatalysis in organic synthesis through four sections: oxidation of alcohols, oxidation of amines, carbon-carbon bond formation reactions, and carbon-hetero bond formation reactions.

1. Introduction

With the intensification of the conflict between the global depletion of fossil fuel and rising energy demand, environmental pollution caused by coal and oil is certainly serious. Therefore, the clean, renewable solar energy resources are gradually entering the scientists' horizons and have shown great advantages in applications in the past decades such as solar cell,[1-3] hydrogen production by water splitting,[4-5] degradation of organic pollutants,[6-9] reduction of carbon dioxide,[10-12] and etc. Meanwhile, application of solar energy as the motive power in organic synthesis starts to become alive.[13-14] The main components of solar energy are ultraviolet (λ=200-400nm), visible light (λ=400-800nm) and infrared (λ>800nm), and the proportion of which are approximately 5%, 43%, and 52% respectively. The ultraviolet energy can directly activate the chemical bonds of some organic molecules to give highly reactive radical intermediates, which results in poor selectivity of the products. Moreover, the infrared wavelength with comparatively low energy is unable to meet the requirement of activation energy for the vast majority of organic reactions.

Visible light is abundant in nature compared to the ultraviolet and infrared, but it generally could not be adsorbed directly by reactant molecules to drive the reaction. Therefore, visible light photocatalyst employed as a bridging media for the energy transfer between visible light and substrates will be of particular importance. Those photocatalysts can be divided into five different groups including the homogeneous photocatalysts represented by Ru, Ir metal complexes,[15-26] organic dye[27-30] and the opposite heterogeneous photocatalysts represented by semiconductors,[31-33] plasmonic-metal nanoparticles[34-35] and other novel photoelectric materials[36-39]. As known to all, heterogeneous visible light catalyst can be easily recovered and the reaction products can be separated more conveniently with respect to the homogeneous ones, so it provides a greener way for the organic chemical transformation.

For the semiconductors with relatively small bang gap like CdS, $BiVO_4$, mpg-C_3N_4, and etc., the catalytic mechanism follows the fundamental principle that the electrons at valence band transit to the conduction band by absorbing photons when the incident visible light energy is equal or greater than the band gap of the semiconductor and hence leaving holes at the valence. Different semiconductors exhibit different band gap width and band positions, so hole and electron pair generated *in situ* have different oxidation and reduction potential. The recombination of hole and electron pairs often occur when the carrier (electron and hole) migrates to the surface of the catalyst, which lowers photo-catalytic efficiency. Several methods have been reported to enhance the separation efficiency of hole-electron pairs such as taking photocatalyst supported on graphene with large surface area[40-41] or to make full use of precious metal material with strong electron conductivity like Pt[42-43] that could accelerate the photogenerated charge transfer. However, not all of the semiconductors with relatively small band gap such as TiO_2, Nb_2O_5 response to the visible light. The most recent research found that even those big band semiconductors were used as photocatalysts under visible light irradiation, they still performed well when specific substrates like benzyl alcohols or benzylamines and its derivatives are used.

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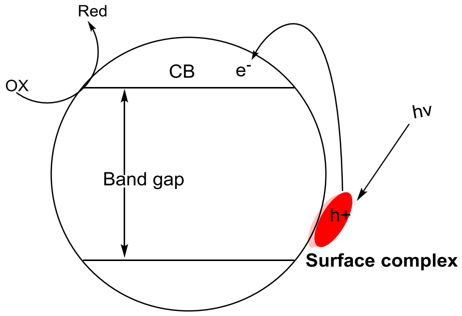
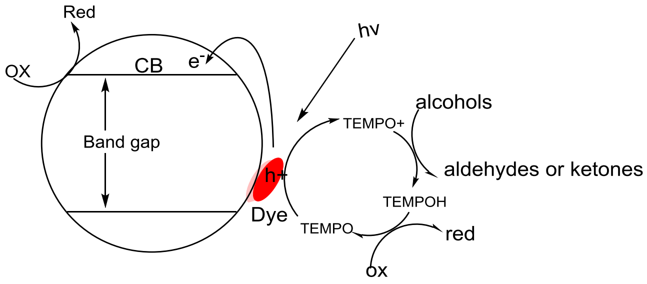
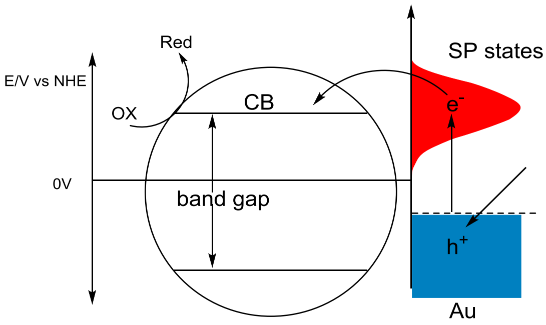


Scheme 1 Schematic diagram for surface complex excited by visible light

In this case, surface complexes formed by the interaction of the active species such as metal active sites[44-46] or surface •OH species[47-48] with alcohols or amines may be the reason that TiO_2 or Nb_2O_5 could response to the visible light, in which these complexes species are more likely excited by visible light and subsequently transfer electrons to the conduction band of TiO_2. Therefore, the visible light photocatalysis principle of TiO_2 and Nb_2O_5 can be depicted as in Scheme 1, which is different to the principle of CdS, mpg-C_3N_4 with small band gap. In another case, Zhao and Robinson[49-51] have recently developed the catalytic systems using dye-sensitized semiconductor as the photocatalyst for the aerobic oxidation of alcohols. The unique catalytic mechanism of dye-sensitized semiconductor photocatalysts in organic synthesis under visible light irradiation is as indicated in Scheme 2. Dye excited by visible light directly injected an electron into the conduction band of semiconductor like TiO_2 and subsequently quenched by TEMPO. Thus the active oxidising species of TEMPO will play a critical role in the oxidation of substrates.



Scheme 2 The process of dye-sensitized semiconductor photocatalyst with TEMPO for oxidation of alcohols[49-51]



Scheme 3 Schematic diagram for the charge transfer induced by Au LSPR effect[32,52]

When the frequency of the incident photon is well matched with the overall vibration frequency of the conduction electrons of the plasmonic-metal nanoparticles, strong absorption of photons is occurred due to the localized surface plasmon resonance (LSPR) effect.[52-53] The plasmon resonance absorption of typical spherical Au nanoparticles is around the 520-550nm visible region, exhibiting great potential in visible-light photocatalysis.[34-35] However, the stability and catalytic performance of the single plasmon nanoparticle is poor, which severely restricts their uses.[32] Generally inert ZrO_2,[54] SiO_2[55] and reducible CeO_2,[56] TiO_2[57] are often used as the supporters of Au nanoparticles. The conduction bands of those supporters receiving electron generated by visible light can excite Au nanoparticles which are subsequently turned into new catalytic active sites (catalytic principle is as shown in Scheme 3).[52] Thus those supporters could not only stabilize plasmon nanoparticles, but also improve the catalytic performance of photocatalyst.

Zhao[32] has reviewed the application of heterogeneous visible-light photocatalysis in the organic transformations based on the types of photocatalysts. We intend to review the processes from different perspective through four sections: the oxidation of alcohols, oxidation of amines, carbon-carbon bond formation reactions, and carbon-hetero bond formation reactions. The application of different types of heterogeneous photocatalysts like metal oxide, metal sulfide, organic semiconductor, plasmonic-metal nanoparticles, and other novel heterogeneous photoelectric materials in organic synthesis will be illustrated in each part.

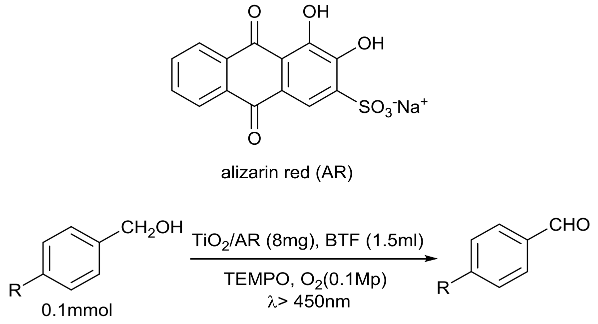
2. Results and discussion

2.1 Oxidation of alcohols

Carbonyl compounds are important intermediates in organic synthesis, the selective oxidation of alcohols is a major approach to obtain carbonyl compound.[58-59] But the traditional chemical oxidants such as chromate[60] or permanganate[61] do not comply with environmental and economic requirements. The low cost, easily available, non-toxic, high active TiO_2 photocatalyst[62-63] using light as the energy source has become a hot research area. However, the big band gap of TiO_2 limits

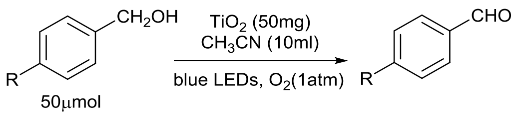
its application in visible-light photocatalysis. Thus modifications of TiO_2[64] such as Fe^{3+}, V^{4+}, Cr^{3+}, Sn^{4+}, and Sm^{3+} metal ion doping,[65-69] C, N, S and F non-metal ion doping,[70-73] or dye-sensitization[49] become necessary to extend photo-response of TiO_2 to visible region.

Zhao et al. reported the selective oxidation reaction of aromatic alcohols catalyzed by the co-catalysis system of dye-sensitized TiO_2 and TEMPO (Scheme 4).[49] Under the visible-light irradiation and in the presence of O_2, the excited alizarin red transferred electrons to the conduction band of TiO_2 and TEMPO subsequently reduced the dye radical cation to complete the dyes photocatalytic cycle. The process was then followed by direct oxidation of alcohols to aldehydes. Robinson et al.[50-51] used the dye/ZnO/TEMPO system with $AgNO_3$ as an terminal oxidant, and successfully oxidized aromatic alcohols to aromatic aldehydes.



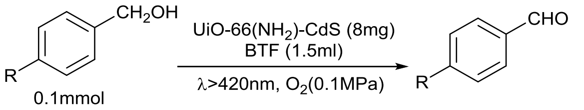
Scheme 4

The unmodified anatase TiO_2 can also catalyze the oxidation of benzyl alcohol and its derivatives in the presence of visible light and O_2, and the visible-light response is derived from the complex formed *in situ* by the interaction between the surface OH species of TiO_2 and alcohols (Scheme 5).[47-48] The 2p orbital of the oxygen atom of the surface complex whose energy level is higher than the valence band of TiO_2 can act as donor energy level,[32] hence the surface complex could be excited by visible light. When the substrate is para-hydroxyl benzyl alcohol, the yield is relatively low. This may be ascribed to the strong adsorption of phenolic hydroxyl with the surface hydroxyl group of TiO_2, resulting in hard desorption and thus excessive oxidation of the products. The adsorption characteristic of the substrate on the surface of TiO_2 is the reason why the relatively low activity of rutile phase TiO_2[74] photocatalyst could also catalyze the selective oxidation of benzyl alcohol to benzaldehyde effectively under the similar conditions. Analogous to TiO_2, Nb_2O_5 also belongs to large band gap semiconductor which can only absorb the light with wavelength λ<390nm. Taking into account of this adsorption characteristic, Tanaka[44] realized the visible-light photocatalytic selective oxidation of alcohols to carbonyl compounds.



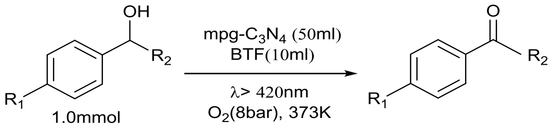
Scheme 5

Though conventional semiconductor TiO_2 photocatalyst can be modified to make it response to visible light, more novel photoelectric materials have been found with better photo-catalytic efficiency. Metal organic framework (MOF) is a kind of porous coordination polymer formed by the self-assembly of metal ion and organic ligand, and recently it has attracted much attention because of its high porosity, specific surface area and other notable properties.[75-77] Use of UIO-66(NH_2)MOFs as the supporter, MOF-CdS nanocomposite was synthesized by Wu.[36] Experimental results indicated that UIO-66(NH_2) could not only acted as a supporter, but also participated in the photoinduced electron transfer, which effectively inhibited the recombination of photogenerated charge carrier, and successfully catalyzed the aromatic alcohol selective oxidation (Scheme 6).



Scheme 6

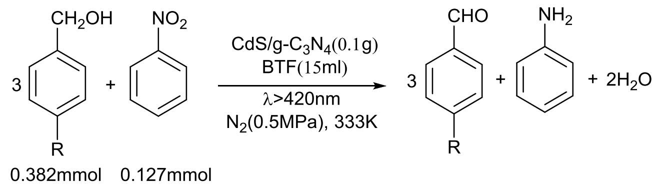
The photocatalyst mpg-C_3N_4 with a medium-band gap and appropriate band positions has been used in selective oxidation reactions.[31] Recently Wang[78] used mpg-C_3N_4 organic semiconductor as a visible light photocatalyst, and successfully catalyzed the oxidation of alcohols to carbonyl compounds under the condition of visible light and O_2 (Scheme 7). The amino and alkaline N groups on the surface of mpg-C_3N_4 are beneficial for the formation of aldehydes and ketones, and the *in situ* generated •OOH intermediate is regarded as the active species.



Scheme 7

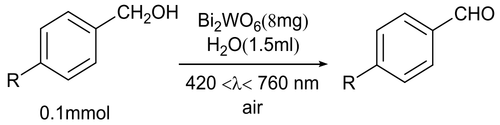
Generally, O_2 is used as an electron acceptor in the photocatalytic oxidative reaction. However, Chen[79] recently reported that aromatic alcohols could be oxidized to aromatic aldehydes using CdS/g-C_3N_4 composite as photocatalyst and nitrobenzene instead of O_2 as an electron acceptor under visible-light irradiation (Scheme 8). The photogenerated hole produced by the excited CdS migrates to the g-C_3N_4 valence band and CdS conduction band receives electron generated by excited g-C_3N_4 at the same time. Subsequently, nitrobenzene was reduced on the surface of CdS, and aromatic alcohols absorbed on g-C_3N_4 were oxidized. Compared with the single CdS or g-C_3N_4 photocatalyst, the conversions and yields in the oxidation of alcohols to aldehydes and the reduction of nitrobenzene reduction to aniline were lower than those with the CdS/g-C_3N_4 composite catalyst. And when the ratio of CdS to g-C_3N_4 was 10%, the catalytic performance was optimal.

Besides, Higashimoto[80] reported that CdS-TiO_2 composite visible light photocatalyst with 15% of CdS could also catalyze the oxidation of benzyl alcohol to benzaldehyde and the reduction of nitrobenzene to aniline simultaneously.



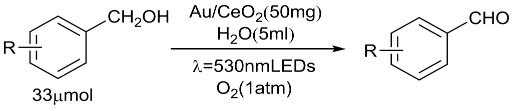
Scheme 8

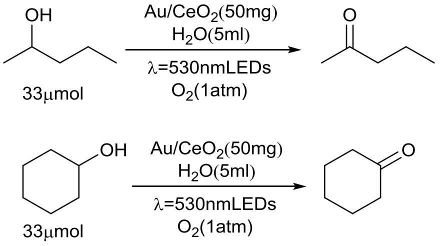
H_2O is regarded as an ideal solvent in organic reaction. However, the problem is that semiconductor valence band hole may oxidize H_2O to form the high active OH radical under the photocatalytic condition, thus the reaction system becomes complicated and uncontrollable. The inherent reduction potential of Bi_2WO_6 photocatalyst valence band is +1.77V vs Ag/AgCl,[79] which is more negative than $H_2O/\bullet OH$ reduction potential. So when Bi_2WO_6 is used as catalyst, water as solvent is feasible. Recently Bi_2WO_6/H_2O/air system was successfully applied to the selective oxidation of benzyl alcohols to corresponding aldehydes (Scheme 9).[81]



Scheme 9

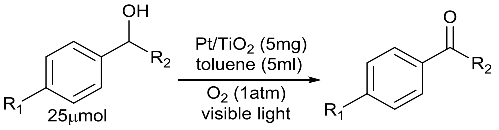
Nanogold plasmonic photocatalyst can also be applied in the light catalytic selective oxidation of alcohols in the visible region due to the LSPR effect of plasmonic nanoparticles. Tanaka[47] successfully realized the selective oxidation of benzyl alcohols under the green light (λ=530nm) radiation by using CeO_2 as the supporter (Scheme 10). In this case, the conduction band of reducible CeO_2 could accept electron from the excited Au nanoparticles, and the as-formed electron-deficient Au can directly catalyze the oxidation of alcohols. Au nanoparticles also possess the ability to decompose the active oxygen species H_2O_2[82] which is generated by electrons injection from the conduction band of CeO_2 into O_2 and preferred to formation of $\bullet O_2^-$ radical formed by one-electron reduction of O_2. So in this system, high selectivity of benzaldehyde may be attributed to the decomposition of the active oxygen species by Au nanoparticles. Except aromatic alcohols, aliphatic alcohols also can be selectively oxidized to carbonyl compounds by Au/CeO_2 visible light photocatalyst,[83] and the chain or cyclic secondary alcohols were oxidized to the corresponding ketones.





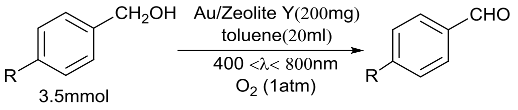
Scheme 10

The process of a hot electron injecting from plasmonic-metal irradiated by visible light into supporter is the critical procedure in organic synthesis under photocatalysis. Hence, the metal/semiconductor interface will play an important role in transferring electron. Recently, Shiraishi reported that Pt nanoparticles could be excited by visible light due to the LSPR effect (Scheme 11).[84] The catalyst with low Schottky barrier and large number of perimeter Pt atoms might be in favour of the electron transferring from Pt to TiO_2 by controlling the amount and size of Pt particles. In addition to this, great effort by Shiraishi was done to increase the efficiency of electron transfer at the metal/semiconductor interface such as Au-Cu and Pt-Cu alloy loaded on anatase TiO_2 etc.[85-88] So, facilitating electron transfer at the interface to improve photocatalytic activity is of research significance.



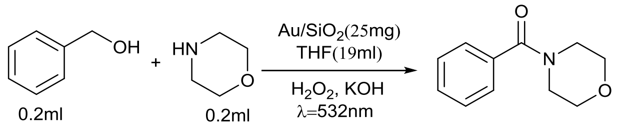
Scheme 11

Recent research revealed the great influence of the property of the substrates on the yield of the product besides the nature of photocatalysts in photocatalysis. For example, Zhang[89] reported that Au nanoparticles supported on Y-type zeolite could catalyze the selective oxidation of aromatic alcohols (Scheme 12). The results showed that regular porous molecular sieve as supporter could gather the reactants, and the conversion was related to the polarity of reactant molecules.



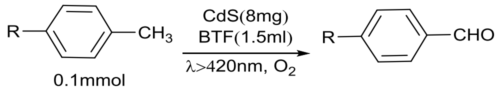
Scheme 12

Different supporters have distinctive effects. When inert SiO_2 was used as the supporter of Au nanoparticles with H_2O_2 as the terminal oxidant, Au/SiO_2 can catalyze the oxidative coupling of benzyl alcohol and morpholine to afford 4-benzoylmorpholine under λ=532nm visible radiation. Benzyl alcohol was first oxidized to benzaldehyde by photocatalysis, then formation of amide compounds took place (Scheme 13).[55]



Scheme 13

The activation condition for the saturated sp^{3}C-H bond is very harsh, which causes difficulty in controlling the selectivity of the reaction. Under visible-light irradiation, cubic phase, sheet shaped semiconductor CdS[90] can catalyze the oxidation of toluene and its derivatives to the corresponding aldehydes (Scheme 14). This CdS has the characteristics of large surface area and high light-induced charge carrier separation efficiency, making the selectivity for aldehyde to 100%. Toluene was oxidized to the corresponding radical cation and O_2 was reduced to the corresponding superoxide radical anion in the CdS valence and conduction band, respectively. Subsequently, two active species were combined to produce benzaldehyde.

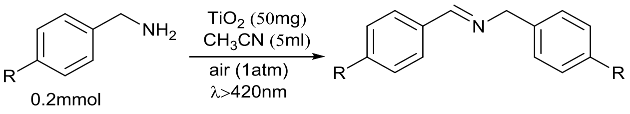


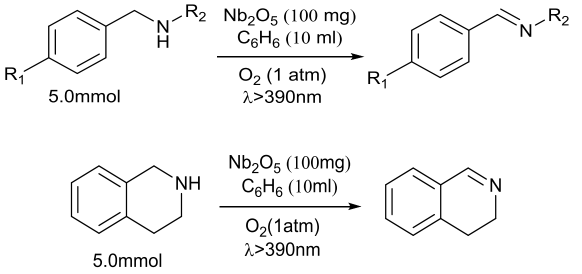
Scheme 14

2.2 Oxidation of amines

The oxidation of amines is a kind of important chemical transformation, and is one of the key steps in the synthesis of drug and pesticide intermediates.[91-92] The stoichiometric strong oxidant, such as 2-iodylbenzoic acid[93] or *N*-tert-butylbenzenesulfinimidoyl chloride[94] is generally required for the oxidation process. Recently heterogeneous visible light photocatalysts are widely used in selective oxidation of amines. O_2 is used as the oxidant to accept electron under the photocatalysis, and this fully embodies the advantages of visible-light photocatalysis.

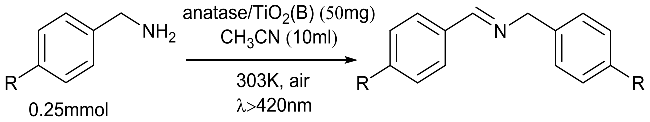
Zhao[45] and Tanaka[46] reported that under the condition of visible light and O_2, TiO_2 or Nb_2O_5 can efficiently catalyze the oxidation of amines (Scheme 15). Although the large band gap of TiO_2 and Nb_2O_5 catalysts limits their applications in the visible region, these catalysts could react with amines to generate surface complex species which are competent in absorbing visible light. The 2p orbital of nitrogen atom of surface complex whose energy level is higher than the conduction band of TiO_2 or Nb_2O_5 can serve as donor energy level. The surface complex were excited by the visible light and transfer electrons to the conduction band of TiO_2 or Nb_2O_5. Based on these, Nb_2O_5 can not only catalyze the conversion of primary amines to the imines, but also act on secondary amines and cyclic amines (Scheme 15).





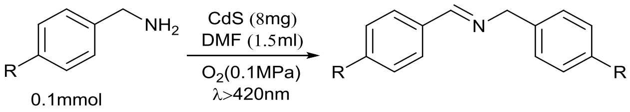
Scheme 15

Compared with other TiO_2 crystal structure such as rutile, brookite, and TiO_2(B), anatase TiO_2 has higher photocatalytic activity.[95] However, the wirelike crystal of mixed-phase photocatalyst composed of 65% TiO_2(B) crystal form and 35% anatase TiO_2 exhibits better efficiency in the catalytic oxidation of amines than single-phase anatase TiO_2 or TiO_2(B).[96] Surface phase junction of TiO_2 mixed-phase photocatalyst facilitated charge carrier separation, and thus improved the photocatalytic activity (Scheme 16).



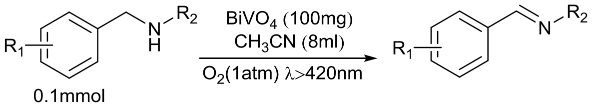
Scheme 16

CdS as a small band gap of semiconductor photocatalyst, without doping and surface modification, could have response in the visible region. Zhang[97] reported the oxidation of benzylamine derivatives to imines by porous single crystal CdS (Scheme 17). High specific surface area and unique crystal surface exposure of the porous single crystal CdS nanocrystals were responsible for the high catalytic activity.



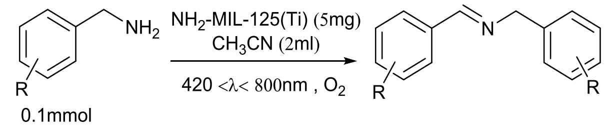
Scheme 17

Although yield of oxidation coupling of primary amines to imines is very high, the oxidation of secondary amines to imines is not efficient by using metal oxides or sulfides semiconductor as the photocatalyst. Recently, Li developed a new Bi-based semiconductor photocatalysts such as BiOCl,[98] $BiVO_4$,[99] for the secondary amines oxidation to imines, the conversion and selectivity could reach more than 93% and 90% respectively (Scheme 18), and under the same condition the effect of TiO_2[45] and Nb_2O_5[46] is poor.



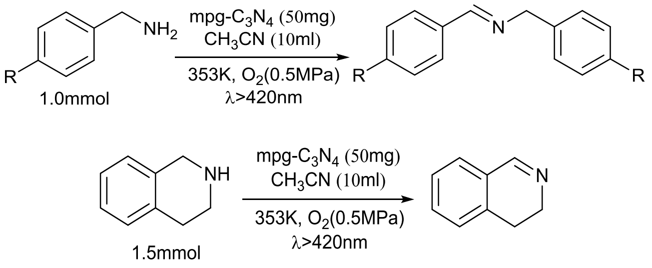
Scheme 18

Novel material MOFs have great potential in the synthesis of imines, and MIL-100(Fe), MOF-253 or other MOFs have been applied to catalytic oxidation of amines.[100-101] Recently, Li[37] reported MOFs NH_2-MIL-125(Ti) could catalyze the oxidation of amines in the presence of visible light and O_2 (Scheme 19). Ti^{3+} species were formed due to the electron transferring from the ligand to the Ti-O oxo-clusters of NH_2-MIL-125(Ti) by LMCT mechanism. Ti^{3+} species were believed to play a very important role in the oxidation of amines.



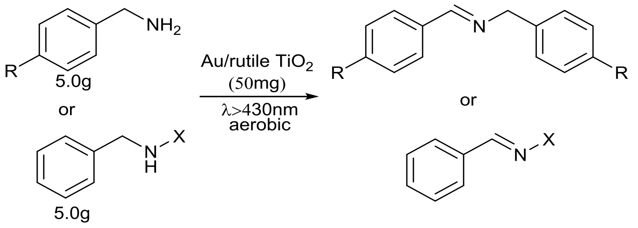
Scheme 19

Wang[102] reported mpg-C_3N_4 organic photocatalyst can catalyze the selective oxidation of the amines. O_2 as the oxidant, primary amines can be oxidatively coupled to form imines at 80℃ and cyclic amine under these conditions can also get good result (Scheme 20). The catalytic performance of mpg-C_3N_4 was better than Nb_2O_5[46] described above. The temperature of 80 ℃ is a necessary condition for high conversion, because the transformation of the amines decreased with the decrease of temperature. When the temperature drops to 30℃, conversion of benzylamines was only 13%.



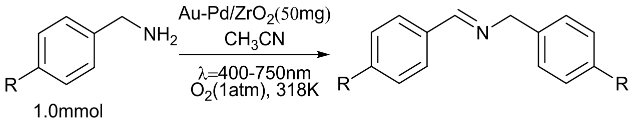
Scheme 20

Use of plasmon Au nanoparticles loaded on the rutile phase TiO_2 as a photocatalyst,[103] the selectivity of the oxidation of amines to imines could reach 99% (Scheme 21). Although the surface complexes can be generated from the interaction of amines with TiO_2 surface and thus resulting in visible-light response, experimental results showed that the *in situ* formed surface complexes of the Au/TiO_2 photocatalysts exhibited very weak absorption in the visible region. Visible-light response is mainly caused by the LSPR effect of Au nanoparticles.



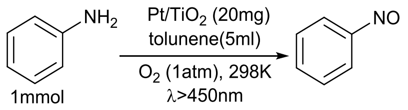
Scheme 21

Electronic heterogeneity of the surface of Au-Pd alloy nanoparticles that stems from the difference of Au and Pd electronegativity causes the surface charge distribution of the Au-Pd nanoparticles to be un-uniform.[104-105] This characteristic is beneficial to improve the interaction between the alloy and the reactant, in which Au nanoparticles serve as plasmonic-metal excited by visible-light, and Pd nanoparticles act as the catalytic activity sites directly. By utilizing this feature, Au-Pd alloy loaded on inert ZrO_2 was applied to the selective oxidation of the amines (Scheme 22).[106]



Scheme 22

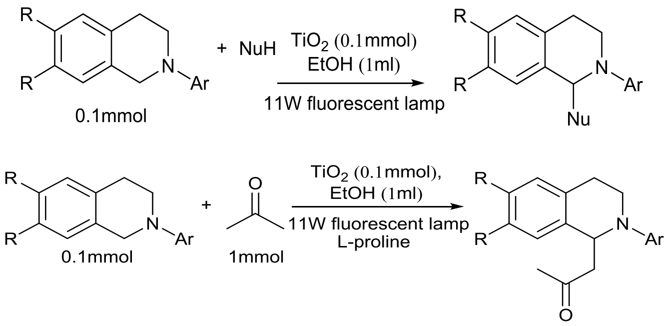
For some organic reactions, the desired products may convert into byproducts when the reaction temperature is high. The oxidation of aniline to nitrosobenzene is a typical example, where aniline and *in situ* formed nitrosobenzene could condense and transform into undesired azobenzene under high temperature.[107] Recently under visible light irradiation, nitrosobenzene was synthesized from aniline by Pt/TiO_2 photocatalyst under the room temperature which is unfavourable to the formation of the azobenzene (Scheme 23).[108]



Scheme 23

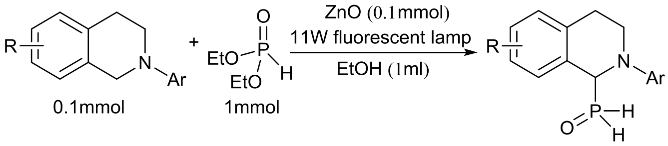
The activation and functionalization of ortho sp^3C-H bond adjacent to nitrogen atom of tertiary amine by photocatalysis is an important pathway for the synthesis of nitrogen-containing compounds. Secondary amines are usually used as substrate in the traditional Mannich reaction,[109] however the photocatalysis based on SET mechanism could use the tertiary amine as the starting material.

Under the irradiation of 11W fluorescent lamp and catalysed by TiO_2, Rueping[110] reported the *N*-aryl tetrahydroisoquinoline derivatives could be oxidized to give iminium ions intermediates which subsequently coupled with nucleophilic compounds such as nitromethane, KCN and etc. (Scheme 24). By the co-catalysis of TiO_2 and L-proline, *N*-aryl tetrahydroisoquinoline derivatives with acetone could also undergo the Mannich reaction. The enamine formed by L-proline with acetone can increase the nucleophilicity of ketone, thereby improving the yield of β-amino ketone.



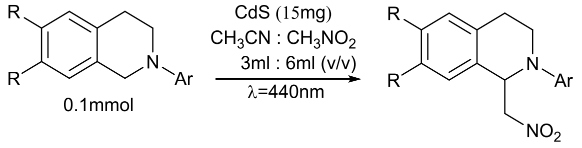
Scheme 24

Excited by visible light, ZnO can also catalyze the activation of the ortho sp^{3}C-H bond adjacent of nitrogen atom of *N*-aryl tetrahydroisoquinoline derivatives (Scheme 25),[110] and then coupled with diethyl phosphite to synthesize high valuable α-aminophosphonate derivatives.



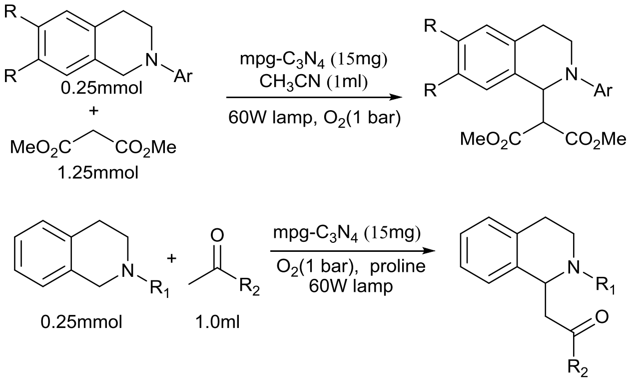
Scheme 25

The choice of solvents sometimes may influence the yield of products. When the polycrystalline CdS as a visible light photocatalyst was applied to the oxidative coupling of *N*-aryl tetrahydroisoquinoline derivatives with nitromethane under the radiation of λ=440nm visible light (Scheme 26), the solvent may be an important factor. Use of nitromethane as a co-solvent (CH_3CN:CH_3NO_2= 1:2) instead of single solvent CH_3CN can effectively prevent the dimerization reaction of benzyl radicals generated by photocatalysis.[111]



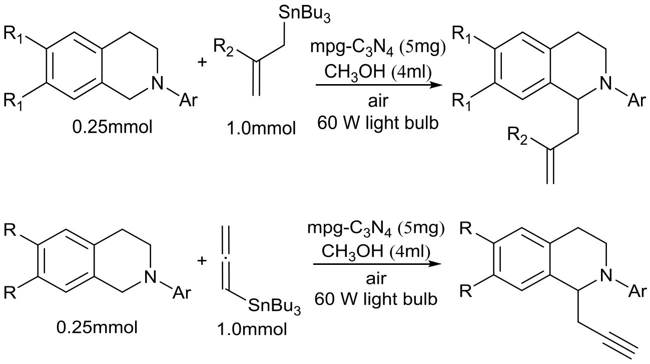
Scheme 26

When mpg-C_3N_4 was used as photocatalyst,[112] higher oxygen pressure was required for the oxidation of tertiary amine to iminium cation, which was then coupled with nucleophiles nitroalkanes or dimethyl malonate (Scheme 27). Mannich-type reaction of tertiary amine and ketone could successfully be performed under the co-catalysis of L-proline and mpg-C_3N_4. Use of 2-pentone with more steric hindrance replacing acetone, the yield dropped sharply to 44%.



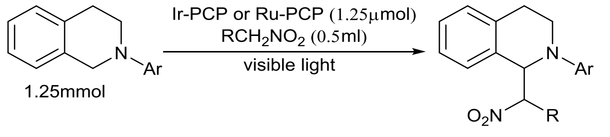
Scheme 27

Generally speaking, for the reaction of iminium cation intermediate and weak nucleophilic reagent, it is difficult to achieve an ideal result. But recently, Blechert[113] realized the coupling reaction of *N*-aryl tetrahydroisoquinoline with the weak nucleophilic allyl or allenyl stannane by using mpg-C_3N_4 as the photocatalyst and air as the oxidant (Scheme 28). Through these improvements such as using air instead of pure oxygen, and methanol as a solvent as well as reducing the concentration of the reaction mixture and excess amount of stannane, all of these measures could increase the collision probability of weak nucleophilic allyl or allenyl stannane with electrophilic iminium cation, and thus greatly enhance the product yield.



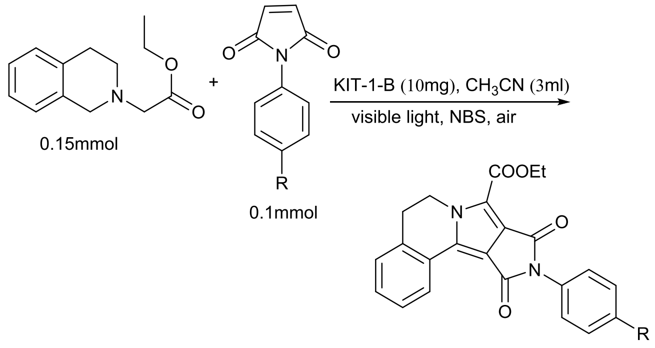
Scheme 28

$Ru(bpy)_3Cl_2$ and $Ir(dtbbpy)(ppy)_2PF_6$ employed as homogeneous photocatalysts to catalyze the aza-Henry reaction has been developed by Stephenson[114] in 2010. Although high yield could be achieved, the drawback of this reaction system is the difficulty in recycling of photocatalysts. The novel porous cross-linked polymers (PCPs) using phosphorescent $[Ru(bpy)_3]^{2+}$ or $[Ir(ppy)_2(bpy)]^{3+}$ as the building blocks designed by Lin[38] can efficiently catalyze the aza-Henry reaction between nitromethane and *N*-aryl tetrahydroisoquinoline under the visible-light irradiation (Scheme 29). This catalyst not only showed the excellent photocatalytic activity, but also can be highly stable, recyclable, which were superior to the homogeneous Ru, Ir complex photocatalyst.



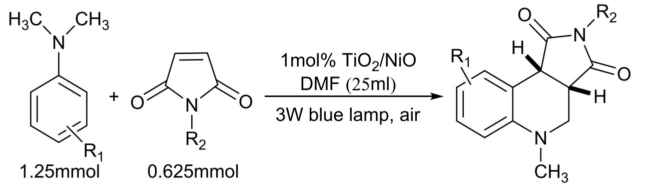
Scheme 29

Zhao[39] reported a new type of KIT-1-B photocatalyst which was synthesized by homogeneous organic photocatalyst iodo-Bodipy immobilized on the siliceous mesoporous molecular sieve KIT-1. Under visible-light irradiation and catalyzed by KIT-1-B, tetrahydroisoquinoline and *N*-phenylmaleimide could undergo [3+2] dipolar cycloaddition reaction to generate pyrrolo[2,1-a] isoquinoline compounds (Scheme 30). The experimental results showed that the immobilization of organic light catalyst did not inhibit single electron transfer between the photocatalyst and substrate and eventually achieved high catalytic performance.



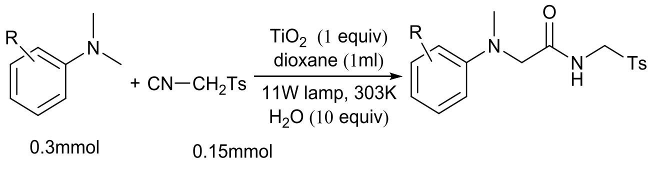
Scheme 30

Besides ion doping and dye-sensitization, surface modification of TiO_2 is another expedient method for extending TiO_2 light response to visible light region. The highly dispersed NiO particles can be used as surface modification agent. NiO/TiO_2 can catalyze the cyclization reaction of *N*,*N*-dimethylaniline derivatives with maleimide (Scheme 31) under the visible-light irradiation.[115] *N,N*-dimethylaniline derivatives were firstly undergone oxidative dehydrogenation by TiO_2 valence band hole to generate α-amino alkyl radical intermediates, which subsequently added to maleimide to produce new radicals, and finally intramolecular cyclization and dehydrogenation to give the target products.



Scheme 31

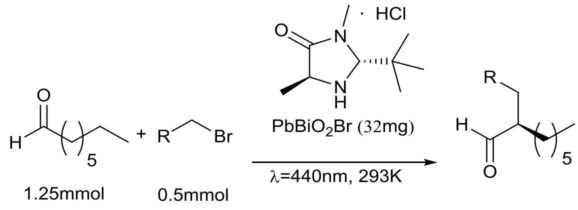
Catalyzed by TiO_2, the α-amino substituted amide compounds could be synthesized through the three components coupling reaction of tertiary amine, isocyanide, and water (Scheme 32).[116] The maximum light absorption wavelength of TiO_2 shifted towards long wavelength due to the interaction of tertiary amine with TiO_2 surface functional group. The strong nucleophilic carbon of isocyanide attacked iminium cation generated by oxidation of tertiary amines, and subsequently hydrolysed to give the product.



Scheme 32

2.3 Carbon-carbon bond formation reactions

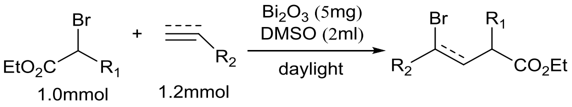
Cross-coupling reaction meet the requirement of atom economy,[117-119] recently photoredox catalysis as a new type of green catalytic method is gradually applied to the cross coupling reaction. The co-catalysis of homogeneous visible light catalyst and chiral amine developed by MacMillan could realize the enantioselective α-alkylation of aldehyde.[120] In order to avoid the use of precious metal homogeneous photocatalyst and succeeding troublesome work-up. Use of suitable semiconductor visible light catalyst $PbBiO_2Br$[121] instead of noble metal catalyst can also catalyze the above reaction with almost same yield and ee value (Scheme 33). At 440 nm light irradiation, photoinduced electron by excited $PbBiO_2Br$ semiconductor transfered to the halogenated carbonyl compounds to generate α-carbonyl radical and bromine anion, then α-carbonyl radical attacked the enamine *in situ* produced by secondary amine chiral catalyst and aldehyde to form α-amino radical which can be oxidized by semiconductor valence band hole to iminium cations, and eventually released the α-alkylation products of aldehyde and organic amine catalyst. When α-bromide carbonyl compounds were used as the alkylation reagent, the combination of semiconductor Bi_2O_3 and organic catalyst can also catalyze the enantioselective alkylation of aldehyde.[122]



Scheme 33

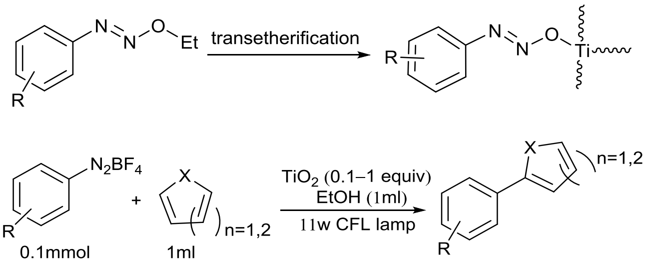
Catalyzed by homogeneous Ru and Ir complexes under visible-light irradiation, the atom transfer free radical addition reaction (ATRA) has been reported by Stephenson.[123] Recently, heterogeneous Bi_2O_3 was used as a ATRA reaction catalyst (Scheme 34).[124] The α-bromide carbonyl compounds were first reduced to alkyl radicals and bromine anion, then radicals attacked the double bond of terminal olefins to form new alkyl radicals. The new generated radicals may proceed in two reaction paths: the first is that radicals were oxidized by Bi_2O_3

valence band hole to form carbonium ion intermediates and subsequently react with bromine anion to give the final products, and the second is the free radical chain growth path which radicals directly capture bromine atom to from α-bromide carbonyl compounds.



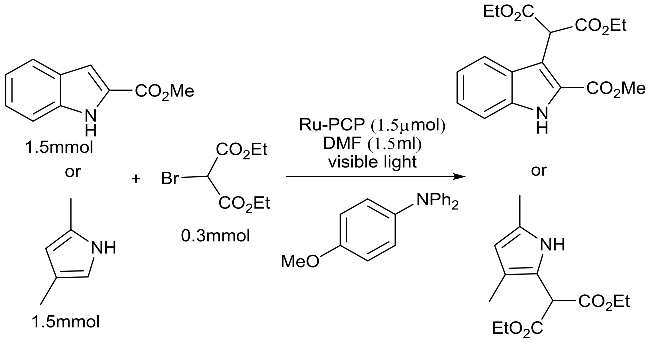
Scheme 34

The direct arylation of heterocyclic compounds such as furan, pyridine and etc. has been implemented in homogeneous photocatalysis system.[125] Recently Rueping[126] used cheaper, non-toxic TiO_2 heterogeneous photocatalyst to realize this reaction (Scheme 35). TiO_2 in this system may play dual role, the first is that TiO_2 as a general thermodynamic catalyst catalyzed the reaction of aryl diazonium salts with ethanol to give azoether compounds which subsequently underwent transetherification to generate TiO_2-azoether species, and these species can be excited by the visible light and transfer electron to TiO_2; The second is as a photocatalyst reducing azoether compounds to generate electron deficient aryl radicals, which added to the heterocyclic giving new free radicals and then transformed into carbonium ion by free radical chain reaction or TiO_2 hole oxidation, and eventually rearomatization to afford the heterocyclic aryl products.



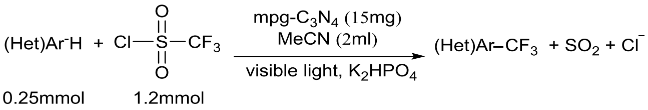
Scheme 35

In the above section, we have discussed the application of the porous cross-linked polymers (PCPs) to the aza-Henry reaction designed by Lin.[38] Besides this, Ru-PCPs could catalyze the α-arylation of bromomalonate (Scheme 36) and oxyamination of 3-phenylpropanal. Moreover, the results showed this photocalyst could be reused several times and still maintain considerably high activity.



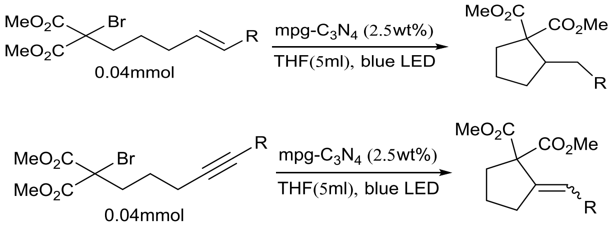
Scheme 36

Fluorine-containing compounds have been widely used in medicine, pesticides, and materials.[127-129] Introducing fluorine atom into organic compounds has been a hot research field in organic synthesis. MacMillan[130] directly introduced the CF_3 group into aromatic hydrocarbons by homogeneous photocatalysis. Subsequently, by using mpg-C_3N_4 as visible light catalyst and CF_3SO_2Cl as CF_3 radical precursor, Blechert successfully achieved the trifluoromethylation of aromatics (Scheme 37).[131]



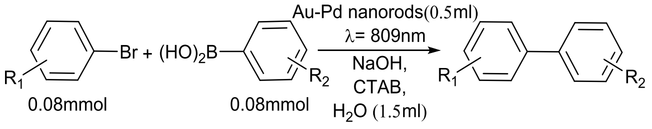
Scheme 37

Stephenson[132] reported the intramolecular radical cyclization reaction of bromide malonic ester with double bonds. Recently, using mpg-C_3N_4 heterogeneous system, this reaction has also been successfully realized (Scheme 38).[133]



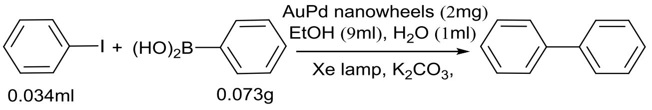
Scheme 38

Palladium as a catalyst is widely used in organic synthesis.[134-135] Palladium catalyzed Suzuki coupling reaction was one of the important methods for the synthesis of biaryls.[136] Recently, Wang[137] found that Au-Pd nanostructures had very good catalytic effect on Suzuki coupling reaction under the irradiation of Xe lamp (Scheme 39). Plasmon nano Au could absorb visible light by LSPR effect, and Pd was used as a direct catalyst for catalytic reaction. Control experiments showed that the light absorption of plasmon nano Au greatly improved the efficiency of the catalytic reaction.



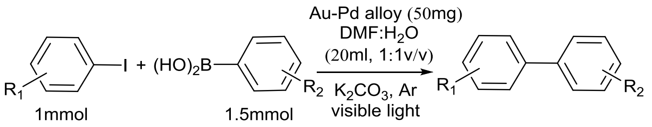
Scheme 39

Huang[138] synthesized AuPd nanowheels with the core-shell structure, where the key characteristic of this material was that Au nanoparticle core were surrounded by Pd. The interaction between Au and Pd was considered to be responsible for the better catalysis efficiency in Suzuki coupling reaction than that of the pure Pd catalyst (Scheme 40).



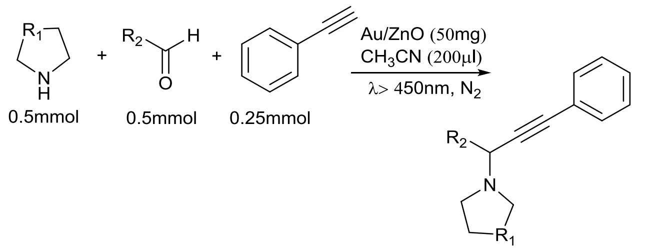
Scheme 40

Au-Pd alloy nanomaterial could also catalyze the Suzuki coupling reaction under the visible light irradiation (Scheme 41). The catalytic efficiency was at optimum when the ratio of Au and Pd is 1:1.62.[139] Furthermore, the application of Au-Pd alloy was not only limited to the Suzuki cross coupling reaction, and it was also proved to have good catalytic activity in others reactions such as Sonogashira, Stille, Hiyama, Ullmann and Buchwald-Hartwig reaction.[140] The co-catalysis of nano Au plasmon and metal Pd is beneficial to improve the conversion and selectivity.



Scheme 41

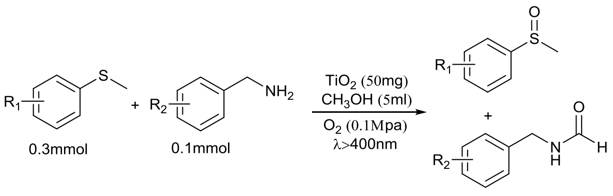
The three components reaction of aldehyde, amine, phenylacetylene to synthesize propargylamines can be realized through the LSPR effect of Au nanoparticles loaded on ZnO supporter under the visible-light irradiation (Scheme 42).[141] Interaction of the supporter and phenylacetylene is a necessary condition for high yield of propargylamines. Compared with TiO_2 and Al_2O_3 as the supporters, the interaction between ZnO and phenylacetylene is stronger which is more favourable for the adsorption of phenylacetylene.



Scheme 42

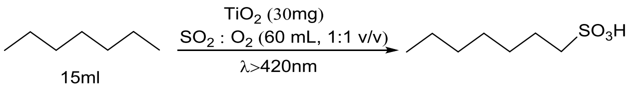
2.4 Carbon-hetero bond formation reactions

The concept of synergistic oxygen-needed photocatalysis has recently been proposed by Lang,[142] in which two seemingly unrelated reactions could be coupled in the same photocatalysis system. For example, by the use of TiO_2 as the photocatalyst, sulfide is oxidized to sulfoxide and amine reacts with methanol to give amide in the presence of O_2 (Scheme 43). By visible-light excitation, the complexes formed by amine adsorption on TiO_2 surface will transfer electrons to the TiO_2 and itself left positive charge oxidizes the sulfide to generate the S-center radical cation surface complex species. Under the action of the oxygen, S-center surface complexes are transformed into sulfoxide and methanol is oxidized to form formaldehyde which reacted with amine to give intermediate, eventually the amide could be obtained by the decomposition of intermediate in the photocatalytic condition.



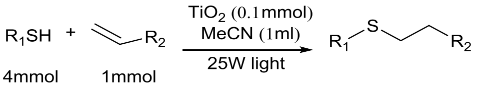
Scheme 43

Using TiO_2 as a photocatalyst, the catalytic oxidation and sulfonation of n-heptane was performed when volume ratio of SO_2 and O_2 was 1:1 (Scheme 44).[143-144] TiO_2 powder exposed to the atmosphere of SO_2 could turn into yellow charge-transfer complex, which had response in the 400~420nm visible region.



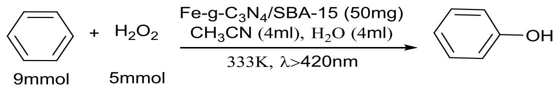
Scheme 44

Thiol-ene reaction is an important method for the construction of C-S bond,[145] although thiol-ene reaction needs be carried out under UV radiation directly. Greaney[146] reported the success of using TiO_2 to catalyze the thiol-ene reaction under visible-light irradiation (Scheme 45). RSH and ROH has analogous physical and chemical properties such as being able to adsorb on the TiO_2 surface to form the complex[68-69] and thus extend the TiO_2 light response wavelength to visible light region. Thiol is oxidized by TiO_2 valence band electron and loses proton to generate RS radical which is then added to double bond of alkene to produce new alkyl radical. Eventually alkyl radical captured the hydrogen of thiol to generate new free radical and the target product.



Scheme 45

Recently Wang[147] reported the use of g-C_3N_4 semiconductor photocatalyst doped by transition metal iron could selectively oxidize benzene to phenol in the presence of H_2O_2 (Scheme 46). H_2O_2 is the donor of the phenolic hydroxyl group, and iron may play an important role in the reduction of H_2O_2 to OH radical. The large surface area of SBA-15 as Fe-g-C_3N_4 supporter also helps to improve the conversion of benzene.



Scheme 46

Conclusions

In short, the application of heterogeneous visible light catalyst in organic reaction is not only confined to the conversion of organic functional groups, but also the catalyzation of the complex carbon-carbon and carbon-hetero coupling reaction. Besides many advantages, heterogeneous photocatalysis is still not ideal from the view of the catalytic activity and selectivity, which thus has limited its application in organic synthesis.

Combination of the advantages of heterogeneous and homogeneous visible light catalyst may be a hot research topic in the future. The high selectivity of the products can be achieved by the synergistic catalysis of different catalysts. For example, the introduction of organic chiral catalyst into the heterogeneous catalysis system can enhance the product's selectivity. At the same time, the design and discovery of new heterogeneous catalyst is also an important direction in the future.

Acknowledgements

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Table of contents

The recent advance of the organic synthesis reactions based on heterogeneous visible-light photocatalysis was reviewed.