

Heterogeneous visible light photocatalysis for selective organic transformations

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The future development of chemistry entails environmentally friendly and energy sustainable alternatives for organic transformations. Visible light photocatalysis can address these challenges, as reflected by recent intensive scientific endeavours to this end. This review covers state-of-the-art accomplishments in visible-light-induced selective organic transformations by heterogeneous photocatalysis. The discussion comprises three sections based on the photocatalyst type: metal oxides such as TiO₂, Nb₂O₅ and ZnO; plasmonic photocatalysts like nanostructured Au, Ag or Cu supported on metal oxides; and polymeric graphitic carbon nitride. Finally, recent strides in bridging the gap between photocatalysis and other areas of catalysis will be highlighted with the aim of overcoming the existing limitations of photocatalysis by developing more creative synthetic methodologies.

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Introduction

One of the challenges in chemistry is the development of renewable energy based processes, to diminish the detrimental

environmental impact associated with chemical industries. Sunlight, being an abundant and easily available energy resource, possesses great potential in driving environmentally benign organic transformations.¹ The introduction of light would shift the apparent thermodynamic equilibrium of redox reactions to favour room temperature chemical synthesis, as well as avoid thermally induced side reactions. Photochemical reactions have also been commonly used as key steps in the synthesis of complicated molecules.² However, low wavelength ultraviolet (UV) light is usually required to drive these reactions,

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and can only be introduced using special reaction vessels. In addition, photochemical reactions typically afford low selectivity of the desired products. To bypass these drawbacks, research has graduated from photochemical to photocatalytic reactions, which can be carried out under milder conditions to obtain higher product selectivity. To this end, a plethora of selective organic transformations on a semiconductor photocatalyst have been developed, which can be performed in common glass reactors.³ Nevertheless, the photocatalyst can only be directly excited by UV irradiation in order to facilitate most of these transformations. The selectivity for the desired product also remains unsatisfactory, due to the involvement of free radical intermediates in UV-induced chemical reactions. This issue is especially acute when attempting selective oxidation of organic compounds with molecular oxygen (O₂). O₂ can be easily attached to free radical intermediates, thus leading to uncontrolled autooxidation products. Not only that the UV-induced hole (h_{vb}⁺) is highly oxidative but also can hence generate a variety of oxygen species to induce the formation of undesired products. Both reasons lead to low selectivity of the desired product.

Due to the aforementioned problems, organic transformations by visible light photocatalysis are favoured in order to facilitate higher selectivity. This also allows for a more efficient utilization of sunlight, which is mostly composed of visible light. However, there exist very few visible light photocatalysts suitable for selective organic transformations. Fortunately, recent discoveries have demonstrated that highly selective redox reactions under visible light irradiation are achievable, with the provision of an appropriate photocatalyst and the right reaction conditions.

Ruthenium or iridium metal complexes and metal free organic dyes have been the subject of recent comprehensive reviews, being excellent homogeneous photocatalysts for a series of organic transformations under mild visible light irradiation.^{1,4} Due to the length limit of this review, these topics will not be covered here, and readers are recommended to refer to the aforementioned reviews for a more in-depth understanding. Herein, the main focus will be on the recent

development of the visible-light-induced selective organic transformations by heterogeneous photocatalysis. It is intended that a balanced point of view be provided by analysing the different approaches to improve selectivity through visible light photocatalysis. The commonalities and dissimilarities of these approaches will be comprehensively covered, serving as a ready-to-use guide for further research on innovative organic transformations under visible light irradiation. This review has been divided into three sections according to photocatalyst type: metal oxide photocatalysts, plasmonic photocatalysts and polymeric graphitic carbon nitride. Each section guides the readers through a series of reactions from the most common to the more niche, while enumerating their reaction conditions and unique features. A discussion will also be provided on the importance of combining the aforementioned photocatalysts with Pd catalysis or organocatalysts, in order to overcome the current limitations of photocatalysis and devise more creative visible-light-induced organic transformations.

Metal oxide photocatalysts

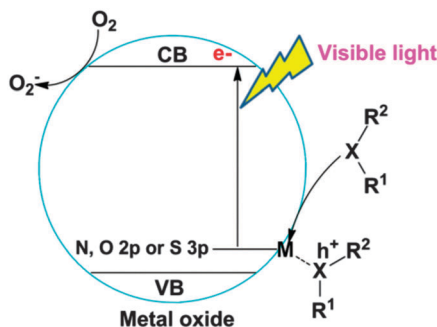
TiO₂, Nb₂O₅ and ZnO are typical large band gap metal oxide semiconductors, which are efficient photocatalysts under UV irradiation. The photocatalytic activity of these metal oxides is usually associated with non-selective free radical reaction processes. Hence, they are widely used for the photodegradation of organic pollutants in water, *i.e.* mediating the total destruction of these pollutants to CO₂ and H₂O with O₂ under UV irradiation. Despite the low selectivity of metal oxides in water, the selective oxidation of alcohols and amines on rutile TiO₂ and Degussa P25 TiO₂ under UV irradiation have been successfully achieved.^{5,6} However, for the majority of organic transformations by heterogeneous photocatalysis, the deployment of organic solvent and visible light irradiation can significantly improve product selectivity. Thus, it is more appealing to use visible light photocatalysis for organic transformations. Surface complexes, formed by the interaction of TiO₂ with colourless molecules containing the carboxyl group, such as ethylenediaminetetraacetic acid⁷ and *trans*-ferulic acid,⁸ or phenolic hydroxyl group, such as fullerol,⁹ could initiate photocatalytic reaction for their own degradation or other redox reactions under visible light irradiation. Arguably, interfacing chemical reactions with commercially available metal oxides is a more convenient route to achieve selective organic transformation under visible light irradiation. Among them, by weak bonding such as surface complexation of substrates, metal oxides could straightforwardly serve as the platform for visible-light-induced organic reactions.

The reaction processes on metal oxides under visible light irradiation are detailed in Scheme 1. Typically, the excitation of an electron from the valence band (VB) to the conduction band (CB) of a semiconductor metal oxide can only be accomplished with UV irradiation due to its large band gap. The heteroatom (X = O, S or N) containing substrates are also unable to absorb visible light directly. However, the heteroatom substrates can easily adsorb onto the surface of metal oxides *via* weak



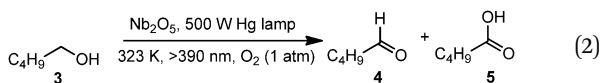
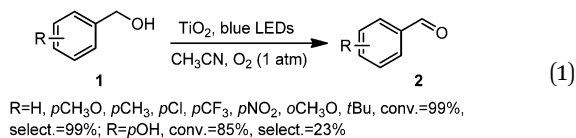
Jincai Zhao

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Scheme 1 Surface complexation heteroatoms (X = O, N or S) on metal (Ti, Nb or Zn) oxide for visible-light-induced reactions.

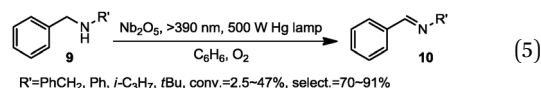
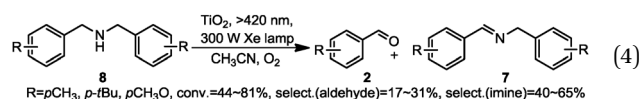
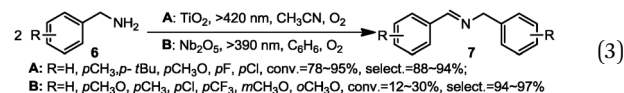
coordination and create new electron donor level above the VB of metal oxide from the 2p orbital of O and N or 2p orbital of S, leading to weak visible light absorbance. As heteroatoms are electron rich atoms which can be easily activated, the electron from the heteroatoms will be smoothly injected into the CB of metal oxide under visible light irradiation, and ultimately transferred to O_2 or other electron acceptors. The positive charge (h^+) localized at the heteroatoms can either induce the activation of the adjacent C–H bond and its subsequent functionalization (in the case of O and N) or the direct functionalization of the heteroatoms (in the case of S) by O_2 or nucleophiles. Such reactions are of great importance as heteroatom containing molecules are important starting materials for the synthesis of bioactive compounds. This mode of activation enables high selectivity even with O_2 as the terminal oxidant, which is challenging to execute under UV irradiation. In summary, the interaction between metal oxide and heteroatom containing substrates could induce visible light absorbance and consequent activation of the substrates, wherein O_2 could either be directly incorporated into the product for oxofunctionalization or simply act as the electron acceptor.



Along this line, the oxidation of alcohols **1** to corresponding carbonyl compounds **2** with O_2 on anatase TiO_2 was achieved under visible light irradiation (eqn (1)).¹⁰ The O-atoms can weaken the adjacent benzylic C–H bond and facilitate substrate adsorption on TiO_2 . Thus benzyl alcohol and its derivatives are very suitable organic substrates for this mode of visible-light-induced activation. Under blue light-emitting diodes (LEDs) irradiation, the selective oxidation of benzyl alcohols with O_2 could be successfully realized on anatase TiO_2 in CH_3CN . Excellent conversions and selectivities were achieved for a series of substituted benzyl alcohols except when the substituent is –OH. This is because the substituted OH group provides

extra coordination sites for interacting with TiO_2 , consequently leading to the destruction of the phenyl ring. Replacing the benzylic C–H with C–D and subjecting the substrates to kinetic studies, a high kinetic isotope effect (KIE) value of 4.2 was obtained, suggesting that the activation of benzylic C–H is the rate determining step for the overall photocatalytic cycle. This indicates that interaction of the –OH groups with the surface of anatase TiO_2 plays a central role in defining the visible-light-induced selective oxidation of benzyl alcohols to corresponding aldehydes.¹¹ Apart from anatase TiO_2 , rutile TiO_2 nanorods have also been used for the aerobic oxidation of benzyl alcohols to benzaldehydes, yielding a high selectivity of 99% under visible light irradiation.¹²

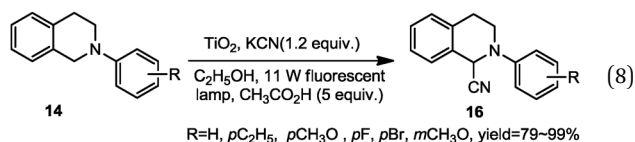
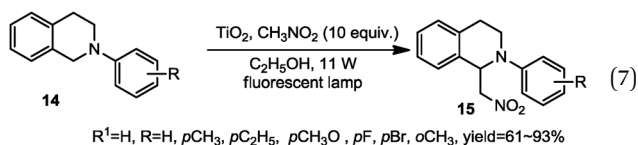
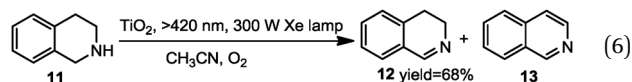
As this mode of visible-light-induced reaction utilizes only the CB of TiO_2 for organic transformations, large band gap semiconductors with a CB position similar to TiO_2 can also be applied to this type of reaction scheme. Other metal oxide semiconductors such as Nb_2O_5 can also serve as a choice platform for visible-light-induced redox reactions. Under solvent free conditions, Nb_2O_5 acts as an efficient photocatalyst for the aerobic oxidation of alcohols.¹³ The mechanism of the oxidation of alcohols has been investigated using Fourier transform infrared spectroscopy, electron spin resonance (ESR) and kinetic studies. Although Nb_2O_5 cannot absorb visible light of wavelengths >390 nm, the aerobic oxidation of 1-pentanol **3** into their corresponding carbonyl compounds **4** and **5** (eqn (2)) is able to proceed under up to 480 nm visible light irradiation, due to the interaction between 1-pentanol **3** and Nb_2O_5 .



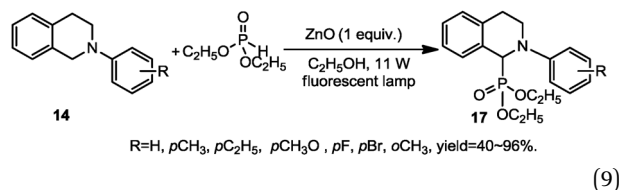
The photocatalytic aerobic oxidation of benzyl amines **6** on Degussa P25 TiO_2 has been recently reported for highly selective formation of corresponding imines **7** under UV irradiation.¹⁴ According to the criteria stated in Scheme 1, benzyl amines are suitable substrates for selective oxidation under visible light irradiation on TiO_2 . High surface area anatase TiO_2 or Nb_2O_5 are both desirable photocatalysts as they offer more coordination sites for amines. This enables the selective formation of imines **7** from primary amines **6** to be successfully achieved under visible light irradiation and CH_3CN or benzene solvent (eqn (3)).^{15,16} Since the benzylic C–H bond adjacent to an N-atom is weaker than that adjacent to an O-atom, atmospheric O_2 can also be directly used as the oxidant for the selective oxidation of amines. Primary benzylic amines have been selectively oxidized to corresponding imines with moderate to good selectivities on

TiO₂. Moderate selectivities for imines were achieved from the aromatic rings containing heteroatoms such as N, O or S. Significant amounts of aldehydes were produced for the oxidation of secondary benzyl amines **8** on TiO₂ under visible light irradiation (eqn (4)).¹⁶ When Nb₂O₅ was used as the photocatalyst for visible light reaction, the reported substrate conversions were relatively low compared to that of TiO₂, but the selectivity was higher. It should be mentioned that the selectivity of imines **10** are even higher when secondary amines **9** are used as substrates (eqn (5)).¹⁶ However small amounts of corresponding aldehydes were also detected using Nb₂O₅ as the photocatalyst.

Another interesting phenomenon to note is that the oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline **11** on TiO₂ afforded 3,4-dihydro-quinoline **12** with a good yield and isoquinoline **13** under visible light irradiation (eqn (6)).¹⁵ This category of substrates are famous for their versatility in weaving new C–C bonds with suitable nucleophiles.

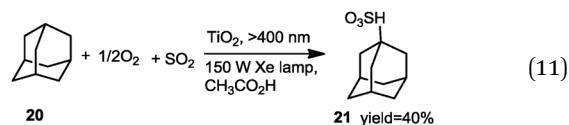
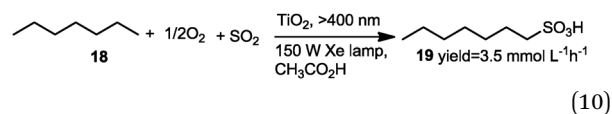


Besides incorporating O₂ into the activated substrates or carrying out dehydrogenation reactions, other nucleophiles have also been incorporated into the activated substrates adjacent to N-atom, enabling even more complicated functionalization under visible light irradiation on Degussa P25 TiO₂. This demonstrates that the surface of TiO₂ can act as a platform for more versatile and selective organic transformations. New C–C bonds were successfully constructed under the mild visible light irradiation of an 11 W fluorescent lamp.¹⁷ Both CH₃NO₂ (eqn (7)) and KCN (eqn (8)) were able to replace O₂ as the nucleophile, facilitating the formation of different C–C bonds to afford **15** and **16** for tetrahydroisoquinoline derivatives **14** in good to excellent yields.

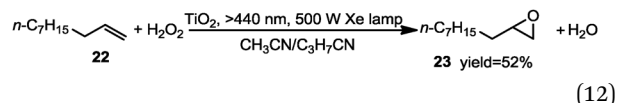


The surface of ZnO, which possesses a similar CB edge to that of TiO₂ and Nb₂O₅, can also act as a platform for

visible-light-induced organic transformations. This has been employed to functionalize the sp³ C–H adjacent to N-atoms in tetrahydroisoquinoline derivatives **14** with diethyl phosphonate to **17** under visible light irradiation (eqn (9)).¹⁷

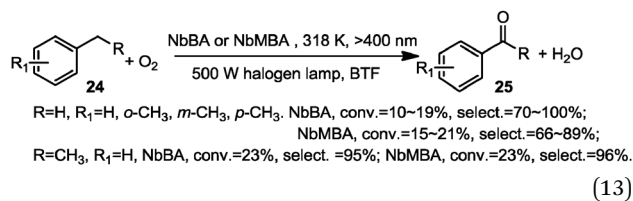


The C–H bonds of alkanes are more stable than those adjacent to heteroatoms. Even worse, without the existence of heteroatoms, the interaction between substrate (alkane **18** or **20**) and TiO₂ will be much weaker. As a result, the direct oxygenation of alkanes with O₂ is impossible under visible light irradiation. By interacting with a reactant containing the heteroatom S, *i.e.* SO₂ with anatase TiO₂, a surface complex will be generated. With this surface complex formed *in situ* as the visible light photocatalyst, the inert sp³ C–H bond of the primary position (eqn (10)), secondary position (cyclohexane) and tertiary position (eqn (11)) can all be converted to value-added sulfoxidation chemicals in the presence of O₂.¹⁸ When exposed to wavelength λ > 400 nm visible light irradiation of a 150 W Xe lamp, the electron transfer from SO₂ to TiO₂ can induce the activation of C–H of alkanes. The resultant alkane free radicals will then react with O₂ and SO₂ to produce the sulfoxidation products (**19** or **21**).



The epoxidation of alkene is a reaction of industrial importance. However, akin to alkanes, alkenes lack the suitable coordination sites present in heteroatom substrates. Therefore, the weak adsorbed alkene substrates are unable to interact with TiO₂ directly to induce visible light absorbance and the ensuing activity. Thus this oxidation reaction cannot use O₂ as the oxidant under visible light irradiation. This hurdle was circumvented by the deployment of H₂O₂ as the terminal oxidant. The visible light active surface complex was formed through the interplay between H₂O₂ and TiO₂. Early in 2001, the epoxidation of 1-decene **22** to epoxide **23** with H₂O₂ was reportedly carried out on a rutile TiO₂ photocatalyst, in the presence of mixed solvents of acetonitrile and butyronitrile when exposed to λ > 440 nm irradiation from a 500 W Xe lamp (eqn (12)).¹⁹ The formation of Ti-η²-peroxide species on the surface of rutile TiO₂ upon treatment with the oxidant, H₂O₂, accounts for the observed visible light photocatalytic activity. The epoxidation of 1-decene **22** with O₂ can be carried out on both anatase and rutile TiO₂. However, λ > 340 nm UV light irradiation was

required for direct excitation of the TiO₂ photocatalyst rather than the surface complex.

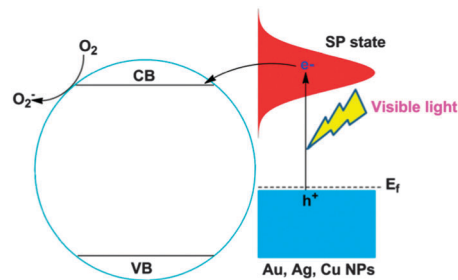


Grafting organic substrates on the surface of niobium hydroxide is another effective method for the preparation of visible light active photocatalysts. The niobium hydroxide grafted with benzyl alcohol (NbBA) or 4-methoxybenzyl alcohol (NbMBA) could be an efficient visible light photocatalyst for the challenging reaction of aromatic alkane oxidation by O₂ in benzotrifluoride (BTF) (eqn (13)).²⁰ This is prepared by the reaction between niobium chloride and anhydrous benzyl alcohol or 4-methoxybenzyl alcohol under solvent thermal conditions. The afforded photocatalyst can render high conversions of the substrates **24** and high selectivity for corresponding aldehydes or ketones **25**. This phenomenon can also be observed for titanate grafted with benzyl alcohol, though with lower activity compared to that of NbBA and NbMBA.

There is a plethora of examples regarding visible-light-induced selective organic transformations on the surface of commercially available metal oxides. However, the reaction is initiated by the excitation of the adsorbed reactant; as a result, the scope of substrates able to undergo such transformations on metal oxides is limited. The challenging activation of a sp² C–H bond in a benzene ring is beyond the capacity of this methodology. In order to accommodate a broader range of organic substrates, one should seek effective photocatalysts which can be directly excited under visible light irradiation. The utilization of the surface plasmon resonance (SPR) effect of nanostructured Au, Ag and Cu paves a delicate pathway towards this goal, which will be elaborated in the following section.

Plasmonic photocatalysts

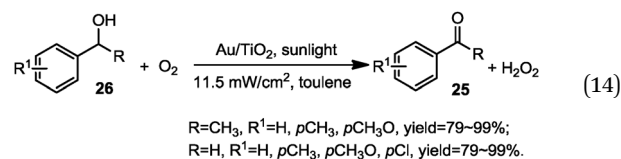
SPR is the collective oscillation of electrons in a solid or liquid, which is stimulated when the frequency of the incident light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. The SPR effect in nanostructured materials is known as localized SPR. The absorbance spectra surface plasmon bands of Au, Ag, and Cu spherical nanoparticles (NPs) display maxima at ~530, ~400, and ~580 nm respectively, which is within the range of visible light. As a result, the localized SPR effect of Au, Ag and Cu NPs may potentially manipulate chemical conversions under visible light irradiation.²¹ The SPR effect of NPs was first examined for the potential photocatalysis of the unselective degradation of organic species in 2008, using Au or Ag NPs supported on ZrO₂ or AgCl under visible light irradiation.^{22,23} This marks the entry of plasmonic photocatalysts into the domain of selective redox transformations under visible light



Scheme 2 Surface plasmonic metal (Au, Ag or Cu) NPs for visible light induced reactions.

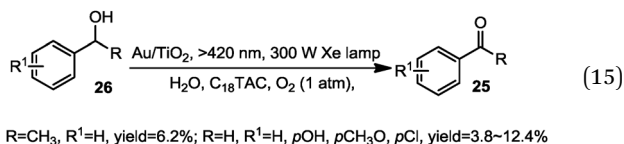
irradiation. Although free standing plasmonic NPs are capable of catalyzing the organic transformation under visible light irradiation, their stability suffers under the photocatalytic conditions. Therefore, for realistic application, most plasmonic photocatalysts are supported on metal oxides.

Reducible metal oxides like CeO₂ or inert supports like ZrO₂, Al₂O₃ or SiO₂ have been reported to enable good performance for plasmonic NPs. In particular, the most popular metal oxide support of choice is TiO₂. The CB of TiO₂ can assist the electron transfer to an electron acceptor such as O₂, which is beneficial for efficient selective aerobic oxidation. The visible-light-induced organic transformation with O₂ by plasmonic photocatalysts is rationalized in Scheme 2. Under visible light irradiation, electrons below the Fermi level (*E_f*) of the plasmonic NPs will be excited to the surface plasmon (SP) states, leaving positive charges (*h*⁺) below *E_f*. Since plasmonic NPs are commonly supported on the surface of metal oxide, the SP state electrons will be injected into the CB of the metal oxide, and ultimately transferred to electron acceptors such as O₂. Meanwhile, the left *h*⁺ would be quenched by the organic substrate to complete the photocatalytic cycle. To comprehensively understand the functionality of a plasmonic photocatalyst, both the properties of plasmonic NPs and metal oxide support should be taken into consideration. In addition to stabilizing plasmonic NPs and shuttling electron transfer, the metal oxides also possess surface acid–base properties, which can facilitate the formation of product for the overall heterogeneous reaction processes. In addition, metal oxide supported Au, Ag, and Cu NPs are excellent heterogeneous catalysts for thermally induced redox conversions, which can facilitate the progress of the plasmonic photocatalysis.

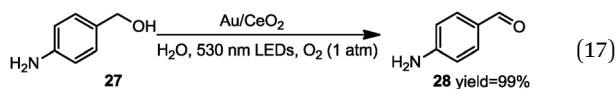
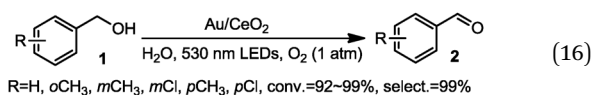


Au NPs of <5 nm diameter loaded at the interface of anatase/rutile TiO₂ (*i.e.* Degussa P25) could serve as plasmonic photocatalysts for the aerobic oxidation of alcohols in toluene under the irradiation of natural sunlight (eqn (14)).²⁴ Au/TiO₂ could act as an efficient photocatalyst when exposed to $\lambda > 450$ nm visible light irradiation from a 2000 W Xe lamp. Au/TiO₂ was prepared *via* the deposition–precipitation method

from H_4AuCl_4 and TiO_2 . Different TiO_2 samples were tested as a support for Au NPs, from which Degussa P25 TiO_2 was proven to deliver the best result. When exposed to sunlight, Au/TiO_2 could prompt the high yield transformation of very dilute alcohols **26** ($2 \mu\text{M}$) into aldehydes or ketones **25** in toluene.

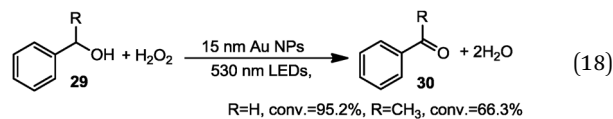


Au/TiO_2 can also act as an efficient photocatalyst for the selective oxidation of alcohol with O_2 in water under the visible light irradiation of a 300 W Xe lamp (eqn (15)).²⁵ The Au/TiO_2 was prepared *via* the deposition-precipitation method from H_4AuCl_4 and TiO_2 . When the cationic surfactant trimethylsteryl-ammonium chloride (C_{18}TAC) was added to the photocatalytic system, the reaction rate was significantly enhanced by 3.3- to 5.7-fold. In a special case, a 29.6-fold increase of the reaction rate could be achieved relative to the surfactant-free system. During kinetic studies, a linear Hammett plot was obtained for the substituted aromatic alcohols **1** to aldehydes **2**. On the other hand, Au/ZrO_2 , which is another photocatalyst based on an inert support, showed no visible light photocatalytic activity as the CB edge of ZrO_2 is too high, thus inhibiting the electron transfer from Au nanoparticles to ZrO_2 .



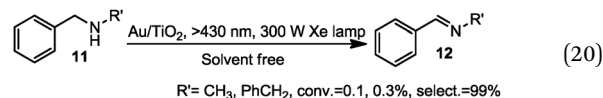
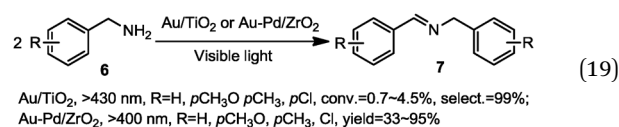
It has been reported that CeO_2 , a reducible metal oxide, could replace the role of TiO_2 as the support for Au NPs. Au/CeO_2 was prepared by photochemical deposition of H_4AuCl_4 on CeO_2 in the presence of citric acid as the reducing agent. The maximum absorption of the obtained Au/CeO_2 is around 550 nm, which is in agreement with the SPR of Au NPs. When exposed to 530 nm LED irradiation, aromatic alcohols **1** can be selectively transformed into corresponding aldehydes **2** with O_2 in water without the assistance of a surfactant (eqn (16)).²⁶ The external surface area of Au NPs plays a crucial role in defining the activity of the photocatalyst. Increasing the average Au particle size to >30 nm affords a very active visible light plasmonic photocatalyst. Au/CeO_2 can also be prepared by the multistep photodeposition method, which leads to larger Au NPs than those prepared by the single-step method.²⁷ Au/CeO_2 can be used for the selective oxidation of 4-aminobenzyl alcohol **27** to 4-aminobenzaldehyde **28** despite the presence of amine functional groups (eqn (17)). The reaction pathway was hypothesized to involve an Au-H intermediate, and ESR has recently been employed to investigate the details of such photo-

induced Au-H reaction of Au/CeO_2 under UV and visible light irradiation.²⁸



The free-standing Au NPs could themselves act as a photocatalyst for the oxidation of alcohols **29** to the corresponding carbonyl compounds **30** with H_2O_2 under 530 nm LED irradiation (eqn (18)).²⁹ Au NPs were prepared from H_4AuCl_4 solution *via* the photochemical method in the presence of benzophenone and a surfactant, yielding a particle size of about 15 nm.

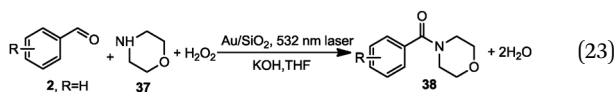
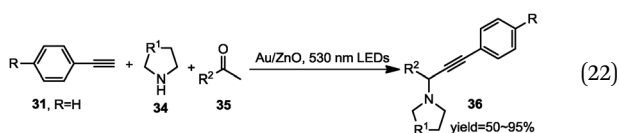
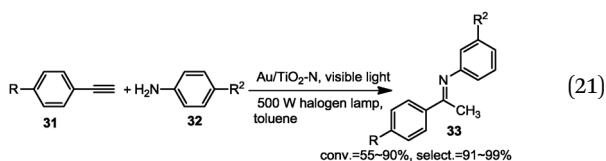
Au NPs alloyed with Pd on ZrO_2 ($\text{Au-Pd}/\text{ZrO}_2$)³⁰ or with Cu on TiO_2 ($\text{Au-Cu}/\text{TiO}_2$)³¹ can enhance the oxidation activity of benzyl alcohols with O_2 exposed to visible light or sunlight irradiation. For $\text{Au-Pd}/\text{ZrO}_2$, the electronic heterogeneity and the distribution of Pd sites at the Au NPs surface play key roles in determining the photocatalytic activity whereas for $\text{Au-Cu}/\text{TiO}_2$, the oxidation and restoration of surface Cu^0 by surface plasmon of Au NPs lead to improvement in electron transfer and prompt the overall aerobic oxidation process.



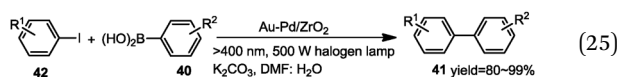
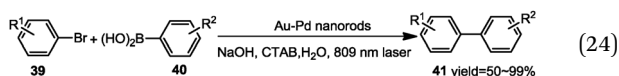
Au NPs with a maximum size of ~ 7 nm supported on the surface of rutile TiO_2 or Au-Pd alloy supported on ZrO_2 ($\text{Au-Pd}/\text{ZrO}_2$) can function as plasmonic photocatalysts for the selective oxidation of primary benzyl amines **6** to imines **7** under solvent free conditions or in CH_3CN (eqn (19)).^{30,32} The aerobic oxidation of secondary benzyl amines **11** to imines **12** was also successful on Au/TiO_2 under visible light irradiation (eqn (20)).³² A variety of binary or tertiary metal oxides including TiO_2 , WO_3 , ZnO , In_2O_3 and SrTiO_3 were tested as the supports, with rutile TiO_2 providing the best results. The aforementioned reactions were all carried out under solvent-free conditions with high selectivity. It should be mentioned, however, that the conversions achieved were very low ($<5\%$).

Both aromatic and aliphatic amines are undeniably very versatile starting substrates for the fabrication of pharmaceutically important and structurally complicated molecules by visible light plasmonic photocatalysis. Imines can also be produced by reacting alkynes **31** with anilines **32** to hydroamination products **33** with Au NPs supported on nitrogen doped TiO_2 ($\text{Au}/\text{TiO}_2\text{-N}$), which serves as the visible light plasmonic photocatalyst (eqn (21)).³³ TiO_2 support delivers better results than other supports. The presence of Ti^{3+} of TiO_2 , arising from nitrogen doping, provides more coordination sites for the alkyne, thereby prompting a better performance than that of pure TiO_2 . Through a similar reaction, propargylamines **36** have been produced by a one-pot synthesis

procedure with the introduction of aldehyde **35** to the amine **34** and alkyne **31** mixture, on the catalyst Au/ZnO under 530 nm LEDs irradiation (eqn (22)).³⁴ The high yields of propargylamines **36** result from the interaction of alkyne **31** with the ZnO support. The use of plasmonic photocatalysts can also be employed to manipulate the oxidative condensation of amine **37** with aldehyde **2** under visible light irradiation. Amide **38** was afforded in tetrahydrofuran (THF) by the oxidation of benzaldehyde **2** and morpholine **37** with H₂O₂ in the presence of a strong base KOH on Au NPs supported on SiO₂ (Au/SiO₂) exposed to 532 nm laser irradiation (eqn (23)).³⁵ Since the selective oxidation of alcohol to aldehyde with H₂O₂ is able to occur under the same photocatalytic reaction conditions, the same amide can be afforded using benzyl alcohol as the starting substrate.

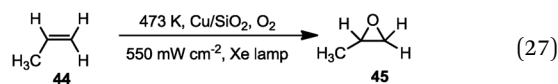
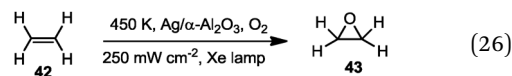


Au alloyed with Pd nanostructures could harvest visible-to-near-infrared light for Suzuki coupling of bromobenzenes **39** and aromatic boronic acids **40** to biphenyls **41** under the irradiation of 809 nm laser (eqn (24)).³⁶ The plasmonic Au nanorods absorb visible light while the Pd shell acts as the direct catalyst for the coupling reaction. The reaction efficiency is dependent on the size of the Au-Pd nanorods, with the smaller nanostructured Au-Pd nanorods delivering the best performance. Suzuki coupling of iodobenzenes **42** and aromatic boronic acids **40** to biphenyls **41** can also be achieved on Au-Pd/ZrO₂ under visible light irradiation (eqn (25)).³⁰ It was similarly concluded that the conduction electron of the SPR Au nanocrystals produces energetic electrons at the surface Pd sites, thereby enhancing the intrinsic catalytic activity of Pd in promoting the coupling reaction. Au-Pd core-shell nanowheels also successfully photocatalyze the Suzuki coupling reaction and oxidation of alcohols with organic peroxides under Xe lamp light irradiation.³⁷



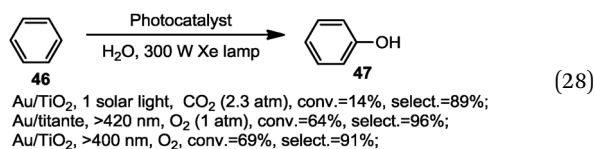
Apart from Au, Ag and Cu NPs can also be used as visible light plasmonic photocatalysts for selective epoxidation of

ethane **42** to ethylene oxide **43** on Ag/ α -Al₂O₃ (eqn (26)) and epoxidation of propylene **44** to propylene oxide **45** on Cu/SiO₂ (eqn (27)) with O₂. Ag nanocubes of ~60 nm edge length supported on α -Al₂O₃ can be used for industrially important processes, *i.e.* the selective oxidation of ethylene to ethylene oxide.³⁸ At 450 K, with the introduction of visible light into the system, the steady-state oxidation rate shows a 4-fold increase relative to that driven by thermal energy only. However, the enhancement rate as a function of temperature decreases from 8-fold at lower temperatures to 3-fold at high temperature without influencing the selectivity for ethylene oxide **43**. Kinetic studies using ¹⁸O labelled oxygen showed a large KIE value of 1.19 ± 0.01 for the photothermal process. The linear dependence of the photo-induced reaction on the light source intensity in addition to the large KIE value indicates an energetic electron-assisted O₂-dissociation process. Cu NPs with an average size of 41 ± 9 nm supported on the inert SiO₂ (Cu/SiO₂) can tune the selectivity for the light-driven epoxidation of propylene **44** (eqn (26)).³⁹ The selectivity enhancement by Xe lamp irradiation is attributed to the localized SPR of Cu NPs which weakens the Cu-O bond, thereby prompting the reduction of Cu₂O to Cu⁰.

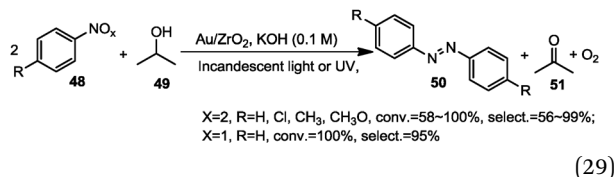


The sp² C-H bond of benzene **46** is more stable than sp³ C-H bonds, which makes its hydroxylation more difficult. Plasmonic photocatalysts are applicable to this type of reactions under UV or visible light irradiation (eqn (28)). 3% Au/TiO₂ was prepared by the reduction deposition of HAuCl₄ on Degussa P25 TiO₂ with NaBH₄ in anhydrous ethanol. Under simulated solar irradiation containing UV light, the aqueous hydroxylation of benzene **46** was performed to afford phenol **47**. Under the oxidizing CO₂ atmosphere, a selectivity of 89% and benzene conversion of 14% were achieved on Au/TiO₂.⁴⁰ Visible-light-induced hydroxylation was also achievable with nanostructured Au prepared under slightly different conditions. Au nanodisk at the interlayer between layers of titanate could serve as a visible light photocatalyst, and was prepared by the modification of layered titanate with (3-mercaptopropyl)trimethoxysilane. The thiol-modified layered titanate was first mixed with HAuCl₄, followed by reduction with NaBH₄. Under visible light irradiation, a remarkable selectivity of 96% for phenol was reported.⁴¹ It should be mentioned that the addition of phenol in the photocatalytic system can enhance both the reaction rate and the product selectivity. Besides the use of NaBH₄, the reduction of HAuCl₄ can also be conducted with ethanol under photochemical conditions. Under UV irradiation in N₂ atmosphere and ethanol solution, the TiO₂ will be reduced by ethanol, and upon adding HAuCl₄ to the reaction system, Au NPs will be loaded *in situ* on

TiO₂. Pt and Ag NPs may also be loaded on TiO₂ *via* a similar method. Such synthesized materials, especially Au/TiO₂, are effective visible light photocatalysts for the hydroxylation of benzene **46** with O₂ in water.⁴²



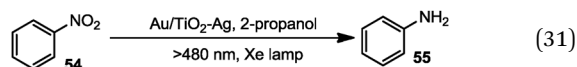
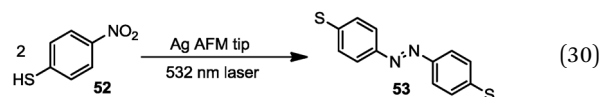
As mentioned previously, Au/ZrO₂ is inactive for the aerobic oxidation of alcohols under visible light irradiation. However, a recent report details the selective reduction of nitrobenzenes **48** into corresponding aromatic azo compounds **50** on Au/ZrO₂ in 2-propanol **49** with KOH as the additive under UV light irradiation in an Ar atmosphere (eqn (29)).⁴³ Au/ZrO₂ was prepared by reduction deposition of HAuCl₄ on ZrO₂ with NaBH₄ in the presence of lysine in H₂O. The resultant Au NPs was about 6 nm in size. It was quite a remarkable finding that in addition to the aromatic azo compounds and acetone **51**, O₂ was concomitantly produced as the co-product in the photocatalytic process. This may serve as a model system to deepen our understanding of the oxidation of water to O₂ during artificial photosynthesis driven by plasmonic photocatalysts.



The overall redox process occurs on the surface of Au NPs under the irradiation of UV-Vis light. Like in the oxidation of alcohols, the surface Au–H plays a pivotal role in the photocatalytic reaction. The key step in the reduction process is the breaking of N–O bonds by the surface Au–H species. Au–H reacts with the N–O bonds, yielding HO–AuNP species which subsequently decompose to yield O₂ and regenerate the H–Au species. The electrophilic N–O bond cleavage is preferred when energetic electrons are present in the environment, as in the case of illuminated Au. As the CB edge of ZrO₂ is too high for electron transfer to occur readily from Au NPs to ZrO₂, ZrO₂ is proposed to play no active redox role in the photocatalytic process other than simply supporting the Au NPs.

With Ag as an SPR photocatalyst, the nanoscale reaction mechanism for the reduction of nitrobenzene **52** to azo compound **53** was monitored with 633 nm laser Raman spectroscopy using Ag coated AFM tips as the photocatalyst under 532 nm laser irradiation (eqn (30)).⁴⁴ Detailed molecular reactions such as monolayer disorder and reactions on a single catalytic site can be directly observed through this method. In fact, Au/TiO₂ with Ag NPs as a co-catalyst is able to photocatalyze the reduction of nitrobenzene **54** to

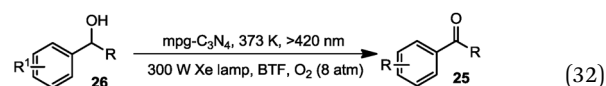
aminobenzene **55** with 2-propanol under visible light irradiation (eqn (31)).⁴⁵



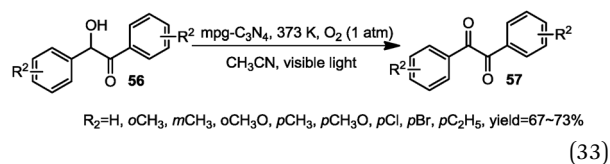
In summary, plasmonic photocatalysts play an essential role in driving versatile selective organic transformations under visible light irradiation. However, the success of these photocatalysts is negated by the fact that they are based on expensive noble metals, such as Au and Ag. Typically, the effective usage of the SPR effect for chemical reactions necessitates relatively large NPs which make the nominal turnover number (TON) in relation to Au, Ag atoms very small. From an economic perspective, earth-abundant materials or even metal free visible light heterogeneous photocatalysts capable of more cost effective visible-light-induced organic transformations need to be discovered. The recently reported polymeric graphitic carbon nitride belongs to this family of inexpensive photocatalysts.

Polymeric graphitic carbon nitride

Polymeric graphitic carbon nitride (g-C₃N₄) is a graphene-like layered material which comprises C, N and H impurities. g-C₃N₄ possesses a band-gap in the medium range and high structural stability under both thermal and photochemical conditions. Due to these properties, g-C₃N₄ can function as a metal-free visible light photocatalyst for selective redox reactions. Large surface areas of this polymer, such as in mesoporous g-C₃N₄ (mpg-C₃N₄), are usually required to boost the reactant to access the reactive photocatalytic sites, which is beneficial for visible-light-induced redox reaction.



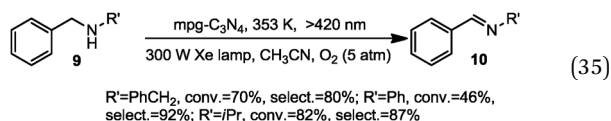
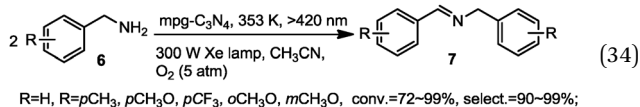
R=H, R¹=H, pCH₃O, pCH₃, pCl, pCOOCH₃, conv.=57–100%, select.=90–99%;
 R=CH₃, R¹=H, conv.=77%, select.=99%;



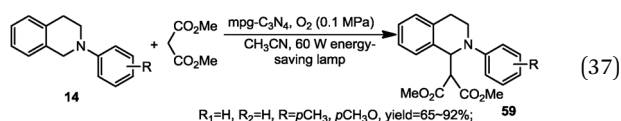
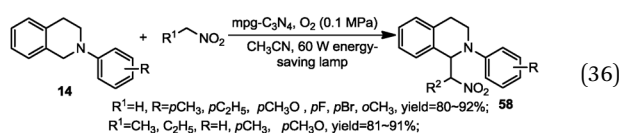
R₂=H, oCH₃, mCH₃, oCH₃O, pCH₃, pCH₃O, pCl, pBr, pC₂H₅, yield=67–73%

Both aromatic alcohols **26** and aliphatic alcohols can be transformed into the corresponding aldehydes **25** with O₂ on mpg-C₃N₄ exposed to wavelengths λ > 420 nm visible light irradiation (eqn (32)).⁴⁶ The mpg-C₃N₄ used was prepared using silica NPs as the template with a high mesopore surface area of ca. 200 m² g⁻¹. The high surface area could enhance the accessibility for both alcohols and O₂, which is the key to success in many heterogeneous catalytic systems. A KIE value of 3.3 has been obtained during kinetic studies, indicating that

the activation of benzylic C–H is the rate determining step. Both electron withdrawing and donating groups enhance the reaction rate for the aerobic oxidation of alcohols, which is strong evidence of a mechanism involving radicals. The solvent plays a very important role in determining both the reaction rate and the product selectivity, and BTF is the best solvent among those tested for this visible light photocatalytic system. The selective oxidation of α -hydroxy ketones **56** to 1,2-diketones **57** was also recently achieved on mpg-C₃N₄ with 1 atm of O₂ in CH₃CN (eqn (33)) under almost identical reaction conditions.⁴⁷

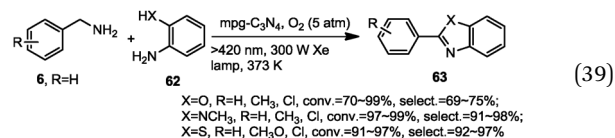


The same mpg-C₃N₄ was employed for the oxidation of primary benzylic amines **6** (eqn (34)) and secondary benzylic amines **9** (eqn (35)) to corresponding imines **7** or **10** with O₂ in CH₃CN under visible light irradiation.⁴⁶ In addition to $\lambda > 420$ nm visible light irradiation, a temperature of 353 K was needed to assist the final product formation. Hammett plot revealed a linear relationship of $\sigma = -0.16$, suggesting the involvement of a cationic carbon intermediate in the reaction process. Kinetic investigation demonstrated that a KIE value of 2.3 was obtained for the oxidation process, implying that the activation of the benzylic C–H bond of amines was the rate determining step.



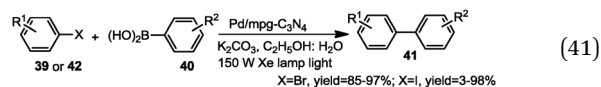
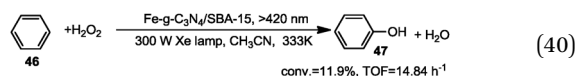
One of the distinct advantages of photocatalytic systems is that the reaction can be carried out at room temperature. In the examples highlighted above, high temperatures were engaged to perform the visible-light-induced reaction, which is a drawback of the mpg-C₃N₄ photocatalyst. However, the selective aerobic oxidation of organic substrates at room temperature was recently reported with mpg-C₃N₄ as a photocatalyst. mpg-C₃N₄ was able to operate as a visible light photocatalyst, without the assistance of an additional additive, for the functionalization of benzylic C–H adjacent to N-atoms with a suitable nucleophile, using 0.1 MPa of O₂ as the oxidant.⁴⁹ Under the visible light irradiation of a 60 W energy-saving lamp, a variety of *N*-aryltetrahydroisoquinolines **14** could be connected with

nitroalkanes (eqn (36)) and dimethyl malonate (eqn (37)) to construct new C–C bonds.



When exposed to $\lambda > 420$ nm visible light irradiation of a 150 W Hg lamp, the oxidation of sulphides **60** to sulfoxides **61** with O₂ can be achieved on CH₃CN with high selectivity (eqn (38)).⁵⁰ The trick is to add 2 equiv. of the additive isobutyraldehyde (IBA) as a free radical initiator to initiate the free radical oxidation.

Molecular structures of greater complexity can be assembled on mpg-C₃N₄ under visible light irradiation. An example is the use of mpg-C₃N₄ can be used for the synthesis of heterocyclic compounds namely benzoxazoles, benzimidazoles, and benzothiazole from benzylamine **6** and *o*-substituted aminoaromatics **62**, whereby an imine intermediate was involved in the formation of products **63** (eqn (39)).⁴⁸ It should be noted that lowering the reaction temperature from 373 K to 353 K will significantly reduce the formation of benzoxazoles, suggesting the importance of temperature during the formation of product.



Like metal oxides, g-C₃N₄ can also serve as the support material for transition metals, the more challenging sp² C–H activation of benzene (eqn (40)).⁵¹ It is interesting to note that both the transition metal and g-C₃N₄ play an active role in the visible light induced hydroxylation of benzene with H₂O₂. This means that the surface area will be a key factor in the heterogeneous catalytic system. Fe-g-C₃N₄ can be supported on ordered mesoporous silica SBA-15 to enhance reactant accessibility, in order to achieve a better photocatalytic activity than in the case of bulk g-C₃N₄. Pd NPs supported on mpg-C₃N₄ may prompt the Suzuki coupling reaction at room temperature, in which mpg-C₃N₄ acts as the photocatalyst whilst Pd acts as the coupling catalyst (eqn (41)).⁵² However, this reaction was driven by the direct irradiation from a 150 W Xe lamp which contains UV light rather than visible light only.

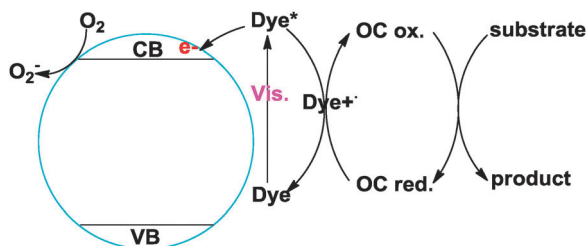
To sum up, the metal-free heterogeneous photocatalyst, g-C₃N₄, manifests itself as an economically viable alternative for organic transformations under visible light irradiation, which includes the selective aerobic oxidation of alcohols, amines, *etc.* However, elevated temperature and high O₂ pressure

were needed in these systems to achieve the desired conversions. As stated previously, it would be ideal to use room temperature and ambient O₂ pressure for visible-light-induced organic synthesis. As an alternative, organic dyes are showing promising photocatalytic activity for selective organic transformations under highly benign conditions. More remarkably, some inactive organic dyes may be transformed to exhibit visible light activity on the surface of metal oxides. Thus a fruitful strategy may be to anchor organic dyes on the surface of heterogeneous catalysts to accomplish the synergetic interplay between the organic dye and metal oxide photocatalyst for creative chemical syntheses.

Dye sensitized heterogeneous photocatalysis

From the aforementioned discussion, it can be concluded that visible-light-induced organic transformation using heterogeneous photocatalysts may be a viable alternative for the environmentally friendly and energy sustainable conversion of industrially important chemicals or the synthesis of delicate bioactive compounds. This area of research may be further expanded to encompass future applications of heterogeneous photocatalytic processes under visible light irradiation. Several lessons can be learnt from the progress in this area of chemical research. Firstly, the dyes that are currently being used successfully in the dye sensitized solar cells can be incorporated directly into photocatalysts for enhancing the visible-light-induced reaction efficiency. Secondly, the intrinsic limitation of photocatalysis can be easily overcome through collaboration with other areas of catalysis. For instance, the otherwise inaccessible enantioselective reactions can be achieved with the addition of an enantioselective organocatalyst. Although heteroatom-containing substrates such as alcohols, amines and sulfides can undergo photocatalytic reactions under visible light irradiation, the addition of organocatalysts may accelerate the reaction.

The detailed reaction scheme for the dye sensitized metal oxide in combination with organocatalysis is illustrated in Scheme 3. An organic dye can absorb visible light to generate an excited state (dye*), which injects an electron into the CB of the metal oxide semiconductor and ultimately transfers it to an electron acceptor, for example O₂, through the CB. Concurrently, the positive charge was left on the dye molecules to produce Dye⁺ free radicals, which can indirectly drive the transformation of the substrate to the product *via* the catalytic cycle of an organocatalyst. In this scenario, the visible light



Scheme 3 Dye sensitized photocatalysis in combination with organocatalysis. OC, organocatalyst; ox., oxidized; red., reduced; Vis., visible light.

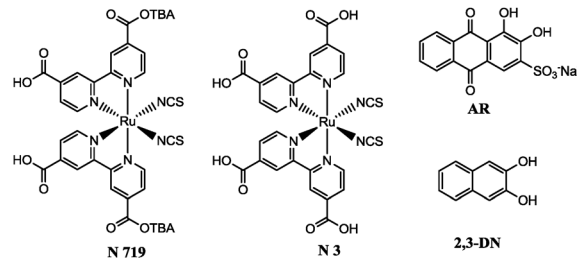
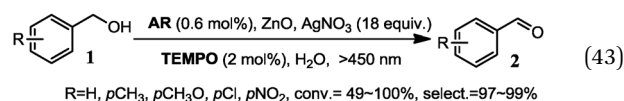
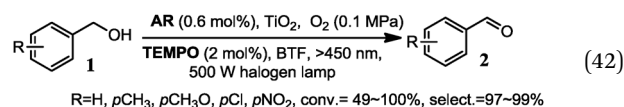


Fig. 1 Organic dyes suitable for anchoring on TiO₂.

absorbance is not limited by substrate adsorption; superior organic dyes serve as sensitizers to absorb visible light more efficiently.

The presence of strong anchoring groups in the organic dyes to form covalent bonding (Fig. 1) can ensure the heterogeneous nature of the photocatalytic system. However, this is not the precondition for this mode of activation. We have learnt that some heteroatom substrates can be smoothly transformed into desired products with the surface of metal oxide as the platform under visible light irradiation. Meanwhile, organocatalysts usually consist of heteroatoms. The substrate may first interact with the organocatalyst to form an intermediate, the heteroatoms of which will interact with metal oxide in a manner similar to that mentioned in the metal oxide section, leading to the formation of the product under visible light irradiation.

A metal free organic dye such as Alizarin Red S (**AR**, see Fig. 1) is photo-inactive for chemical conversions on its own. However, it is able to sensitize metal oxide, making it active under visible light to drive a redox reaction. With the assistance of an organocatalyst, **TEMPO** (see Fig. 2), **AR** can be used to sensitize TiO₂ for visible-light-induced oxidation of alcohols **1** to aldehydes **2** with O₂ in BTF (eqn (42)),⁵³ whilst sensitization of ZnO with **AR** for the same reaction with AgNO₃ can also occur in water (eqn (43)),⁵⁴ which are in agreement with the description in Scheme 3.^{53,54}



Combining TiO₂ with organocatalysts **a** and **b** (see Fig. 2) may be an efficient way for the formation of new C–C bonds

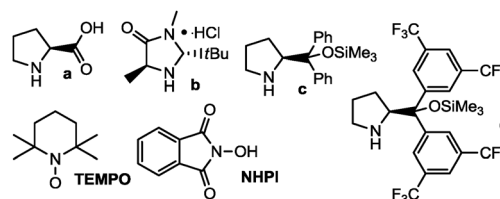
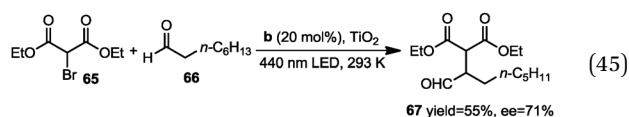
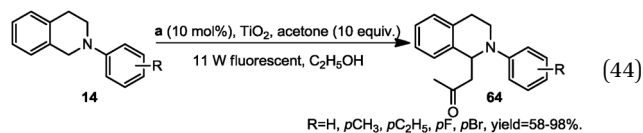
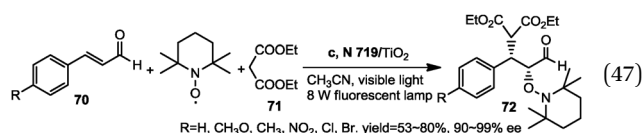
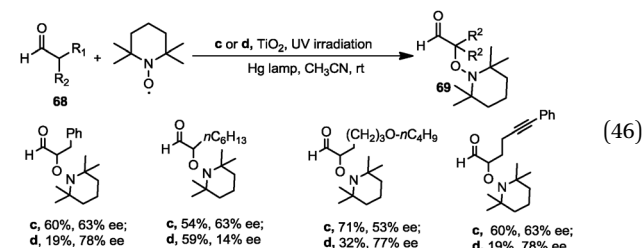


Fig. 2 Organocatalysts used in combination with photocatalysts.

with a ketone or an aldehyde under visible light irradiation.^{17,55} The reaction is initiated by interacting the surface of TiO₂ with the tetrahydroisoquinoline substrates **14** or organocatalyst **a** to afford the product **64** (eqn (44), see Scheme 1 for a more detailed explanation). The reaction rate of enantioselective α -alkylation of aldehydes **66** with TiO₂ and organocatalyst **b** can also be enhanced when the reaction is carried out in a microreactor, underpinning the importance of reactor design for the practical application of organic transformations by heterogeneous photocatalysis under visible light irradiation (eqn (45)).



Meanwhile, combining TiO₂ with organocatalysts **c** or **d** (see Fig. 2) may produce an efficient system for the α -oxyamination of aldehydes **68** with TEMPO to corresponding products **69** under UV irradiation. Due to the lack of visible light absorbance for the individual components and the potentially weak interaction with TiO₂ to induce visible light activity, the reaction needs to be performed under UV irradiation. Such radical coupling reaction is initiated by the single electron transfer to $h\nu_{\text{vb}}^+$ of UV excited TiO₂ (eqn (46)).⁵⁶ The consequential reaction steps are then controlled by organocatalysis, affording highly enantioselective products. Since TEMPO is an excellent organocatalyst for the oxidation of alcohols, the tandem oxidation of alcohol to aldehydes **68** and ensuing asymmetric α -oxyamination of aldehydes **68** can also be achieved through the strategy of combining TiO₂ photocatalysis and organocatalysis.

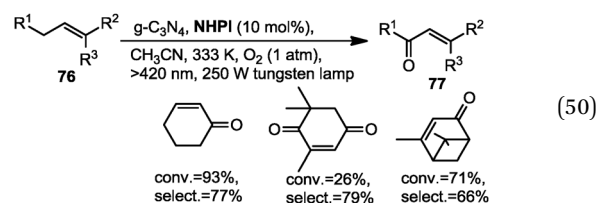
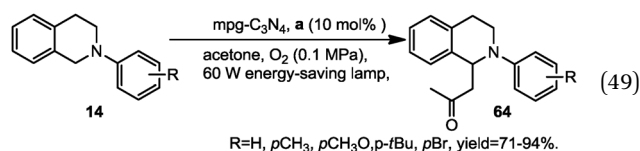


Using the same underlying principle, the aforementioned reaction protocol may be upgraded to conduct redox reactions under visible light irradiation, with the aid of Ru metal complex organic dye **N719** (see Fig. 1). The strong anchoring carboxyl groups in the ligand can immobilize **N719** on the surface of TiO₂, which acts as the initiator for the redox relay involving

organocatalysts **3** as the redox mediators, in order to drive the overall product **72** formation processes under visible light irradiation. The TiO₂ sensitized with organic dye **N719**, together with organocatalysts **3**, can dictate the extremely complicated reaction scheme involving one-pot Michael additions of malonate **71** to α,β -unsaturated aldehydes **70** followed by α -oxyamination of the resulting β -substituted aldehydes, producing good yield and excellent enantioselectivity of the product under visible light irradiation (eqn (47)).⁵⁷

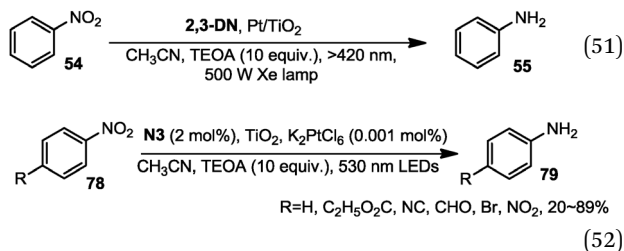


Likewise, efforts have also been expended to anchor the Ru(bpy)₃²⁺ (bpy, 2,2'-bipyridine) complex on SiO₂ encapsulated Ag (Ag@SiO₂) for the selective aerobic oxidation of alkenes **73** to ketone **74** and epoxide **75** with O₂. A TON of 861 with regards to the substrate was obtained when exposed to $\lambda > 400$ visible light irradiation from a 500 W Xe lamp (eqn (46)).⁵⁸ This successfully demonstrates that the combination of both molecular photocatalyst (Ru(bpy)₃²⁺) and plasmonic photocatalyst (Ag@SiO₂) can be adopted to establish new reaction regimes under visible light irradiation.



The combination of mpg-C₃N₄ with organocatalysts **a** (see Fig. 2) can be an efficient way for the formation of new C-C bond product **64** from tetrahydroisoquinoline derivatives **14** with acetone and the presence of O₂ as additional electron acceptor, under visible light irradiation and using acetone solvent (eqn (49)).⁴⁷ The g-C₃N₄ photocatalyst combined with the organocatalyst **NHPI** (see Fig. 2) can effectuate the selective oxidation of an allylic position of alkenes **76** with O₂ to product **77** under visible light irradiation (eqn (50)).⁵⁹ The selective visible-light-induced oxidation allylic position in a complicated molecule with O₂ on g-C₃N₄ and **NHPI** combination was proven to be successful too. This protocol is also applicable to the oxidation of alkanes and alkenes under visible light irradiation, *i.e.* the oxidation of phenylethylene and toluene to benzaldehyde or the oxidation of alkanes (cyclohexane and ethylbenzene) to ketones (cyclohexanone and acetophenone) with O₂. As in most cases where g-C₃N₄ is employed as the

photocatalyst, a relatively high temperature is needed to drive the oxidation reaction in addition to visible light irradiation.



A visible light absorbing surface complex can also be formed when the colourless organic molecule, 2,3-dihydroxynaphthalene (2,3-DN, see Fig. 1) is adsorbed on the surface of anatase TiO₂ *via* the strong bonding of the *ortho* dihydroxyl on the aromatic ring. When used in combination with a common reduction co-catalyst Pt NPs, the surface complex could photocatalyze the reduction of nitrobenzene **54** to aminobenzene **55** with triethanolamine (TEOA) when exposed to $\lambda > 420$ nm visible light irradiation from a 500 W Xe lamp (eqn (51)).⁶⁰ The combination of a metal complex organic dye with a TiO₂ photocatalyst could efficiently reduce nitrobenzenes **78** to aminobenzenes **79** with TEOA under visible light irradiation (eqn (52)). An organic dye N3 (see Fig. 1) in combination with TiO₂ (Degussa P25) along with the assistance of Pt NPs, produced *in situ* from K₂PtCl₆, can effectively reduce nitrobenzene into aminobenzenes with TEOA when exposed to the visible light irradiation from 530 nm LEDs.⁶¹ Interestingly, without the presence of K₂PtCl₆ as the reducing co-catalyst, the reaction rate for the reduction of nitrobenzene to aminobenzene could be augmented by adding trace amount of urea derivatives as the co-catalyst, which is ascribed to the provision of additional proton shuttling channels by urea derivatives.⁶²

Conclusions

Apart from offering easy separation of the photocatalyst from the reaction system, heterogeneous photocatalysis, which interfaces chemistry with materials science, possesses a unique position in the advancement of selective organic transformations under visible light irradiation. Heterogeneous photocatalysis has been flourishing with the recent collaborative efforts of chemists and material scientists, culminating in the development of environmentally friendly and energy sustainable strategies for selective redox organic synthesis. The specific selective redox organic transformations in which these catalysts are applicable include: (1) the oxidation of alcohols, amines, alkene and alkanes or the hydroxylation of aromatic compounds with O₂; (2) the C_α-H bond activation and functionalization with nucleophiles to construct new C-C or C-X (X = O, N or S) bonds; (3) the reduction of nitrobenzenes to corresponding aminobenzenes or azo benzenes with sacrificial agents under O₂-free conditions. The strategy for the exploring of visible light photocatalysts includes the reinventing of old materials such as metal oxides and polymeric carbon nitride with new mechanistic insights, and the creation of new materials such as plasmonic photocatalysts. There are both advantages and disadvantages for different types

of photocatalysts. Metal oxides are stable and inexpensive, but they suffer from a limited scope of substrates and limited range of visible light absorption as the reaction is induced by weak interaction of substrates and metal oxide. For plasmonic photocatalysts, the scope of substrates is relatively broadened. However, plasmonic photocatalysts are more expensive, the reported conversions of substrates are mostly very low and the mechanistic insights are still lacking. g-C₃N₄ is not expensive, but demands high temperature and O₂ pressure in addition to visible light when carrying out most reported transformations. Dye sensitized heterogeneous photocatalytic processes are promising in many aspects, but the stability of the applied dyes under aerobic conditions can be an important concern. Notwithstanding, the disadvantages could be got around by ingenious design.

Heterogeneous photocatalysis can be further optimized and diversified for visible-light-induced selective organic transformations by employing the following tactics: (1) the progress of different branches of photocatalysis could interact with each other to inspire new discoveries; (2) the scope and the efficiency of these reactions could be amplified by the combination of heterogeneous photocatalysts with molecular photocatalysts; (3) the interplay between heterogeneous photocatalysis and Pd catalysis or organocatalysis could broaden the scope of reactions even further to Suzuki coupling or enantioselective reactions, *etc.* The investigation into redox transformations of organic compounds by heterogeneous photocatalysis could deepen our understanding of the photo-induced interfacial electron transfer processes, which in turn have a far-reaching impact on the development and implementation of feasible artificial photosynthesis for solar energy capture and storage. Although significant progress has been made in this area of research, great challenges still need to be resolved before sunlight can be a viable source of energy. More exciting discoveries can be conceived in the pursuit of a green and renewable chemical future. Hopefully, this review can stimulate new insights and creative solutions, thereby carrying forward the visible-light-induced selective organic transformations by heterogeneous photocatalysis to fulfil their potential applications.

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