

Selective Aerobic Oxidation Mediated by TiO₂ Photocatalysis

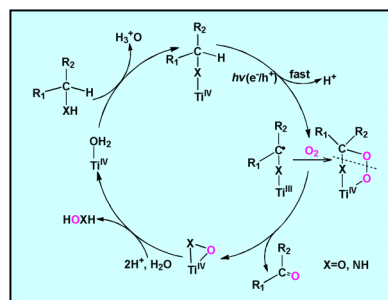
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CONSPECTUS

TiO₂ is one of the most studied metal oxide photocatalysts and has unparalleled efficiency and stability. This cheap, abundant, and non-toxic material has the potential to address future environmental and energy concerns. Understanding about the photoinduced interfacial redox events on TiO₂ could have profound effect on the degradation of organic pollutants, splitting of H₂O into H₂ and O₂, and selective redox organic transformations. Scientists traditionally accept that for a semiconductor photocatalyst such as TiO₂ under the illumination of light with energy larger than its band gap, two photocarriers will be created to carry out their independent reduction and oxidation processes. However, our recent discoveries indicate that it is the concerted rather than independent effect of both photocarriers of valence band hole (h_{vb}⁺) and conduction band electron (e_{cb}⁻) that dictate the product formation during interfacial oxidation event mediated by TiO₂ photocatalysis.



In this Account, we describe our recent findings on the selective oxidation of organic substrates with O₂ mediated by TiO₂ photocatalysis. The transfer of O-atoms from O₂ to the corresponding products dominates the selective oxidation of alcohols, amines, and alkanes mediated by TiO₂ photocatalysis. We ascribe this to the concerted effect of both h_{vb}⁺ and e_{cb}⁻ of TiO₂ in contribution to the oxidation products. These findings imply that O₂ plays a unique role in its transfer into the products rather than independent role of e_{cb}⁻ scavenger. More importantly, e_{cb}⁻ plays a crucial role to ensure the high selectivity for the oxygenation of organic substrates. We can also use the half reactions such as those of the conduction band electron of TiO₂ for efficient oxidation reactions with O₂. To this end, efficient selective oxidation of organic substrates such as alcohols, amines, and aromatic alkanes with O₂ mediated by TiO₂ photocatalysis under visible light irradiation has been achieved.

In summary, the concerted effect of h_{vb}⁺ and e_{cb}⁻ to implement one oxidation event could pave the way for selective oxofunctionalization of organic substrates with O₂ by metal oxide photocatalysis. Furthermore, it could also deepen our understanding on the role of O₂ and the elusive nature of oxygen species at the interface of TiO₂, which, in turn, could shed new light on avant-garde photocatalytic selective redox processes in addressing the energy and environmental challenges of the future.

1. Introduction

Since the discovery of splitting of H₂O into H₂ and O₂ on TiO₂ electrode under UV irradiation in 1972,¹ the photocatalytic reactions on TiO₂ have been under extensive investigation. This is in part because TiO₂ is an inexpensive, earth abundant, nontoxic material that has the potential to address the environmental and energy concerns of the future.² TiO₂ is the most studied metal oxide photocatalyst with unsurpassable stability and efficiency, which holds great promise in areas such as environmental benign organic synthesis,³ degradation of toxic pollutants,⁴ and

production of H₂⁵ under UV or visible light irradiation. In the early years of research in this field, great expectations were placed on selective redox reactions of organic substrates mediated by TiO₂ photocatalysis.⁶ Specifically, the oxidation of alcohols,⁷ amines,⁸ cyclohexane,⁹ and aromatic alkanes¹⁰ with O₂ mediated by TiO₂ photocatalysis under UV irradiation formed the nucleus of studies. However, significant effort in this area was later redirected to degradation of organic pollutants due to the difficulty in selectivity control in valence band hole (h_{vb}⁺) induced free radical reactions in the presence of O₂.

It is traditionally accepted that illumination with light of energy greater than that of the band gap of metal oxide photocatalysts like TiO₂, generates two photocarriers: an electron is excited into the conduction band of the semiconductor, leaving a positively charged hole at the valence band. The geminate photocarrier pair will effect independent reduction (an electron is transferred into the empty acceptor orbital from the catalyst conduction band) and oxidation (an electron is donated from the filled donor orbital to recombine with the hole at the valence band edge) processes.¹¹ However, our recent findings of an oxygen transfer pathway for the oxidation of organic substrates with O₂ led us to conclude that the concerted effect of both h_{vb}⁺ and conduction band electron (e_{cb}⁻) results in the formation of oxygenation products. Especially, e_{cb}⁻ localized at the conduction band of TiO₂ plays a crucial role in determining both the reaction rate and product selectivity. These findings in combination with recent results of the proton coupled electron transfer phenomena in the reduction of organic substrates on TiO₂ give us a more complete picture of the concerted effect of both h_{vb}⁺ and e_{cb}⁻ during an oxidation or reduction event that occurs at the interface of TiO₂.¹²

We started out our investigation on the selective oxidation of organic substrates mediated by TiO₂ photocatalysis partly because it can provide an environmentally benign yet economically viable alternative for organic oxidation reactions. Such transformations are enabled by the most abundant oxidant (O₂) and an inexpensive metal oxide (TiO₂) under ambient pressures and temperatures. We found that selectivity control mediated by TiO₂ photocatalysis, which is substrate dependent, is possible by tuning the reaction conditions (e.g., the selection of solvent, interface engineering such as surface modification to change the adsorption mode or electron transfer pathway, control of the excitation light wavelength, the match of redox potentials, and the introduction of redox mediators).

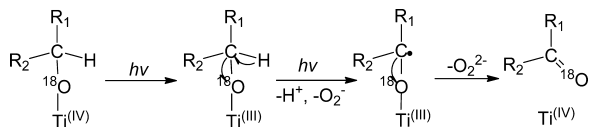
In this Account, we will delineate our recent effort to achieve a better understanding on the intricate role of O₂/e_{cb}⁻ in TiO₂ photocatalysis under controlled reaction conditions. We first introduce the investigation on the aerobic oxidation of alcohols with isotope labeling along with surface spectroscopic techniques to uncover an oxygen transfer pathway, suggesting the concerted effect of both h_{vb}⁺ and e_{cb}⁻ to execute an oxidation event. Directed by these findings, we expanded scope of substrates and, furthermore, realized visible-light-induced selective aerobic oxidation of organic substrates mediated by TiO₂ photocatalysis.

2. Aerobic Oxidation of Organic Substrates on TiO₂ under UV Irradiation

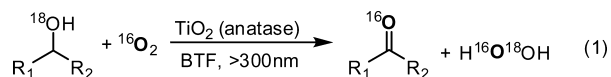
The initial step for the photocatalytic reactions of organic substrates is the adsorption of the organic molecules onto the surface of TiO₂, which is well established by a series of surface techniques.¹³ We just borrow these commonly accepted models for this discussion. The focus here is on the oxidation events of organic substrates with O₂ occurring at the interfaces of TiO₂, in an attempt to have greater insight into the molecular mechanism via product analysis, kinetic studies, and surface techniques such as Raman spectroscopy and diffuse reflectance UV–visible (DR-UV–vis) spectroscopy. Especially, the complicated molecular reaction pathways of the oxidation processes mediated by TiO₂ photocatalysis can be elucidated by isotope labeling starting molecules (substrates or ¹⁸O₂) and monitoring their evolution over time with mass spectrum. Thus, the selective oxidation of alcohols with O₂ mediated by TiO₂ photocatalysis was chosen as the probe reaction while the products were followed by gas chromatography–mass spectrometry (GC-MS) for a better understanding of reaction mechanism.

The selective oxidation of alcohols into corresponding aldehydes or ketones is one of the most important transformations in organic chemistry. However, toxic and stoichiometric oxidants such as Mn(VII) and Cr(VI) are typically required to perform this transformation. Thus, the use of O₂ is preferred to achieve an environmentally friendly oxidation of alcohols. Fundamentally, the photocatalytic oxidative adsorption and stepwise dissociation of methanol, which is the simplest alcohol bridging the oxidation of H₂O and organic compounds, have been under intensive investigation by several convincing surface techniques.^{14,15} The sequential formation of methyl formate on rutile TiO₂(110) surface by oxidation of methanol under UV or 400 nm visible light irradiation was well understood in great detail very recently.^{16–18} However, these discoveries were all carried out under ultrahigh vacuum conditions in which the influence of O₂ was irrelevant to the formation of products. Selectivity control could be one of the most important concerns for aerobic oxidation. For complete conversion of an alcohol molecule, a two-electron transfer is needed. The traditional mode of TiO₂ photocatalysis suggests that O₂ simply plays the role of e_{cb}⁻ scavenger rather than being directly transferred into the product (Scheme 1). The h_{vb}⁺ carries out its independent role for the oxidation of alcohols, while O₂ performs its independent role as electron acceptor.

In order to unravel the origin of the O atoms in the final oxidation products during the selective oxidation of alcohols

SCHEME 1. Two-Electron Transfer for the Aerobic Oxidation of Alcohol According to Traditional TiO₂ Photocatalysis

with O₂ mediated by TiO₂ photocatalysis, we used an ¹⁸O isotope labeling experiment by GC-MS to trace the oxidation process with benzotrifluoride (BTF) as the reaction medium. The O atoms in alcohols such as benzyl alcohol and cyclohexanol were ¹⁸O isotope labeled. The results are summarized in eq 1 with almost 100% of O atoms in aldehyde or ketone from ¹⁶O₂ at different alcohol conversions.¹⁹ The origin of the O atoms in the products is from the oxidant, ¹⁶O₂, rather than from the substrate alcohol itself. BTF was selected as the solvent based on its superior ability to dissolve O₂, which is helpful for the selective oxidation reaction, whereas the oxygen transfer phenomenon holds for reaction carried out in other inert solvents such as CH₃CN and CH₂Cl₂. This is different from noble metal complex catalysis systems, wherein a two-electron transfer from the substrate to O₂ occurs mediated by the oxidase-like Pd complex, leaving O atoms of alcohols intact in aldehydes or ketones.²⁰ The scenario is more like that of oxygenases in enzyme catalysis, which mediate O atom transfer from O₂ to the organic substrates. Note that the corresponding carbonyl compounds were obtained with >99% selectivity at 65% conversion of benzyl alcohol. The overoxidation of benzyl alcohol into 5% benzoic acid occurred only at a very high conversion of 94%, while the selectivity to benzaldehyde was 94%. No overoxidation of cyclohexanol could be observed with a selectivity of 98% to cyclohexanone at 93% conversion.

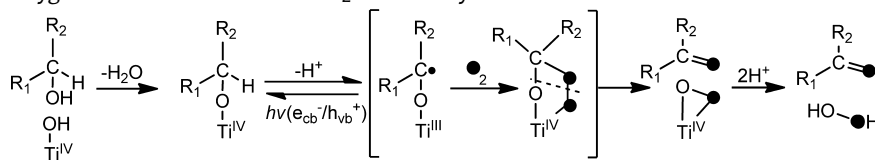
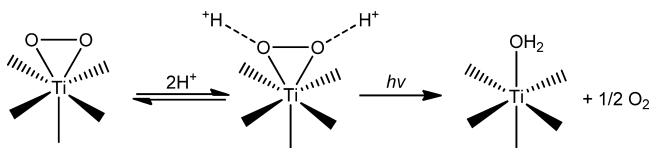


With further investigation with kinetic studies and surface Raman techniques aided with isotope labeling, a *side-on* peroxide species was uncovered on the surface of TiO₂. With this information at hand, the mechanism was proposed as in Scheme 2. A turnover of alcohol to aldehyde or ketone necessitates two-electron transfer. After the $h\nu_{\text{vb}}^+$ induces formation of the Ti^{III}OC*R₁(R₂) intermediate, the transfer of the second electron becomes pivotal to determine the selective formation of product, in which the e_{cb}^- plays an essential role in preventing the autoxidation. The concerted effect of both $h\nu_{\text{vb}}^+$ and e_{cb}^- contributing to the oxidation

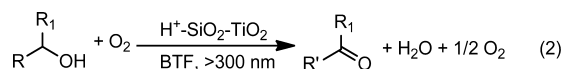
event explains the direct O atom transfer from O₂ into the substrates with high selectivity, highlighting the importance of the second electron transfer process.

However, to achieve the goal of potential application of oxidation reactions by TiO₂ photocatalysis at ambient O₂ pressure and room temperature, a delicate balance between reactivity and selectivity is required. The kinetic issue still represents a major challenge in future practical utilization of these systems. Directed by Scheme 2, we wanted to discern the rate-determining step of the photocatalytic cycle aimed at enhancing the reaction rate. During the Raman spectroscopy investigation, we could directly observe that the Raman shift of Ti *side-on* peroxide (890 cm⁻¹) shifted to 866 cm⁻¹ during ¹⁸O isotope labeling (Raman shift of 24 cm⁻¹), suggesting that it might hold the key to further improving the reaction rate. The decomposition of Ti *side-on* peroxides via heterolysis of the O–O bond would be greatly facilitated by the loaded H⁺ because the protonation of peroxide remarkably weakens the O–O bond (Scheme 3).²¹ Diffuse reflectance UV–visible adsorption (DR–UV–vis) spectra could also observe the presence of the Ti *side-on* peroxide with absorption peak $\lambda_{\text{max}} \approx 410$ nm. Additionally, we used DR–UV–vis spectra to follow the reaction kinetics of the surface Ti *side-on* peroxide species upon Brønsted acid treatment (red-shifted to $\lambda_{\text{max}} \approx 421$ nm). The results demonstrate that the decomposition of the surface Ti *side-on* peroxide species could be accelerated by adding H⁺ into the reaction systems, suggesting the regeneration of TiO₂ surface assisted by acid treatment under UV irradiation.²²

On the basis of this mechanistic insight, we found that loading small amounts of Brønsted acids onto the surface of anatase TiO₂ significantly accelerated the reaction rates of oxidation of alcohols with O₂ without influencing their high selectivities. Motivated by this positive result, we hypothesized that SiO₂ incorporated TiO₂ (SiO₂–TiO₂) would be a more suitable candidate for this kind of improvement since the incorporation of SiO₂ species into TiO₂ could enhance its adsorption capacity for Brønsted acid. We prepared SiO₂–TiO₂ using a sol–gel method by hydrolysis of titanium(IV) *n*-butoxide and tetraethyl orthosilicate and subsequent sintering at 430 °C. Then, the obtained SiO₂–TiO₂ was treated with Brønsted acid (H⁺–SiO₂–TiO₂), conferring almost 100% enhancement of the aerobic oxidation rates of benzyl alcohols with very high selectivities (87–100%) of corresponding carbonyl compounds at high conversions (85–100%) (eq 2).²² The grafting of SiO₂ species on anatase TiO₂ could enhance its activity for degradation of pollutants under visible light irradiation.²³ However, the increase of activity upon SiO₂

SCHEME 2. The Proposed Oxygen Transfer Process in the TiO₂ Photocatalytic Aerobic Oxidation of Alcohols**SCHEME 3.** H⁺ Assisted Decomposition of Surface Peroxides under UV Irradiation

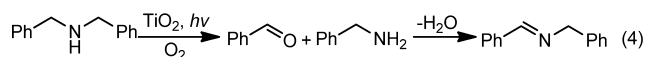
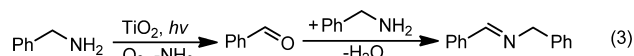
incorporation is quite limited in the selective oxidation of alcohols without the loading of Brønsted acids. These results indicate that the simple acid treatment of the surface of TiO₂ could be an effective way to improve the overall efficiency for selective aerobic oxidation mediated by TiO₂ photocatalysis.



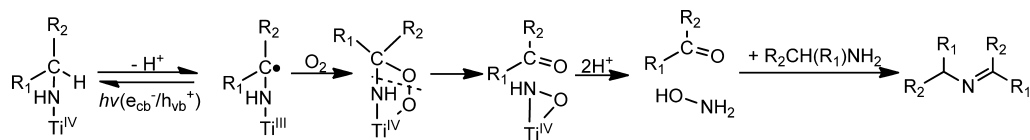
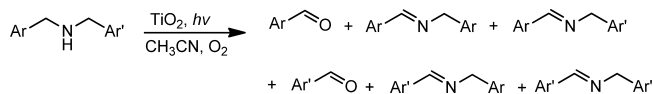
If the concerted effect by $h\nu_{\text{vb}}^+$ and e_{cb}^- of TiO₂ for oxidation of alcohols could work for other organic substrates, more versatile selective aerobic oxidation reactions could be envisioned and achieved, which, in turn, could prove the generality of the oxygen transfer pathway in TiO₂ photocatalysis. Amines were chosen as the probe substrates to test this hypothesis.²⁴ The selective aerobic oxidation of amines is more challenging due to the more active nature of amines compared with alcohols. As a result, the selective formation of targeted products could be more difficult due to undesired side reactions. Under the guidance of Scheme 2, we can easily deduce that the oxidation of amine with O₂ should follow a similar mechanism to form the corresponding aldehyde under UV irradiation, while the formation of imines is a facile process due to the easy nucleophilic attack of the nascent aldehyde by amine (Scheme 4). Significantly, the amine substrates are more versatile than alcohols. Thus, we could choose or design amine molecules with special structural properties. With the analysis of the product distribution, we could have the opportunity to provide more evidence of the O atom transfer from O₂ to amines, which, in turn, could further prove the generality of the oxygen transfer pathway mediated by TiO₂ photocatalysis.

When benzylamine and its derivatives were chosen as the substrates for oxidation with O₂ on Degussa P25 TiO₂

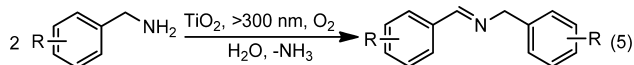
under UV irradiation, high selectivities (71–92%) of corresponding imines were achieved at high conversions (77–99%), in line with the design principle (eq 3). During the O atom transfer process, aldehydes were the intermediates rather than the final products and hence evaded direct detection for primary benzylic amines. Thus, secondary benzylic amines were chosen as the substrates to provide evidence of the O atom transfer from O₂ to amine substrates mediated by TiO₂ photocatalysis. If the same mechanism was in play, significant amounts of corresponding aldehydes should be detected as the final products for the oxidation of secondary benzylic amines (eq 4).¹⁷ During the C–N single bond breaking and the following C=N double bond making process, part of the newly generated benzyl amine could be further oxidized with O₂ into benzaldehyde (eq 4). Indeed, we found significant amounts of aldehydes (12–24%) in addition to imines (38–53%) for the oxidation of dibenzylamine and its derivatives at 70–95% conversions.



Furthermore, when different asymmetric dibenzylic amines are selected as the substrates, there should be four different imines produced and two accumulated aldehydes as the final products. In good agreement with eqs 3 and 4, an exchange of the substituted groups in the imines should occur during the C=N double bond making processes after the breaking of C–N single bonds in the asymmetric dibenzylic amines (Scheme 5). Two aldehydes and four imines with molar ratio near 1:1:1:1 were in the final products at 90% conversion. These results suggest that all the final products were dominated by the oxygen transfer pathway mediated by TiO₂ photocatalysis. In essence, like the oxidation of alcohols, the concerted effect of both $h\nu_{\text{vb}}^+$ and e_{cb}^- controls the selective oxidation of amines into imines on Degussa P25 TiO₂ under UV irradiation, while e_{cb}^- of TiO₂ could also prevent the autoxidation of activated amine species to render the highly selective imine formation via aldehyde intermediates.

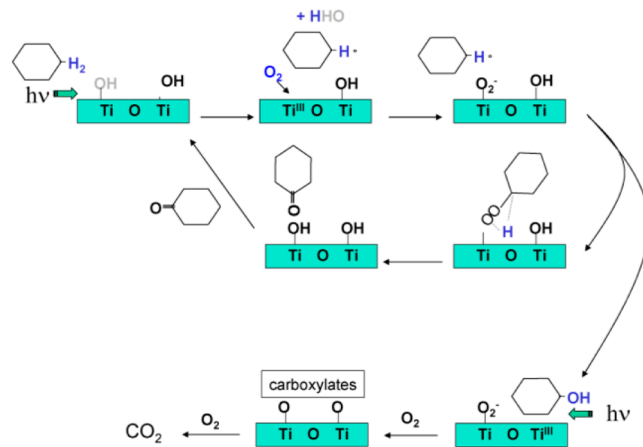
SCHEME 4. Selective Formation of Imines by Photocatalytic Aerobic Oxidation of Amines on TiO₂**SCHEME 5.** Photocatalytic Aerobic Oxidation of Asymmetric Dibenzyl Amines on TiO₂

We further exploited another strategy by the deployment of H₂O for highly selective oxidation of amines to imine with O₂ based on the solubility difference in H₂O of amines (soluble) and imines (insoluble). The formed imines could be easily precipitated from H₂O to avoid secondary destruction in the TiO₂ photocatalytic system. In this manner, we could achieve imine selectivities of 56–94% at amine conversions of 22–40%; imine selectivities of 52–83% at amine conversion of 59–86% on Degussa P25 TiO₂ in H₂O exposed to >300 nm UV irradiation with atmospheric O₂ as the terminal oxidant (eq 5).²⁵ With 4-methoxybenzylamine as the substrate, 0.32 g (51% isolated yield) of imine was afforded as the isolated product by filtration.

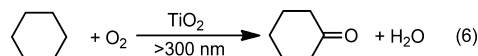


Unlike alcohols and amines, alkanes lack the coordination with the Lewis acid site of TiO₂. It is of great interest to investigate the oxidation of alkanes with O₂ mediated by TiO₂ photocatalysis in acetonitrile under UV irradiation. The liquid phase aerobic oxidation of cyclohexane is of major importance for the production of cyclohexanone and cyclohexanol (K/A-oil). Especially, a high K/A-ratio is desired for the production of ϵ -caprolactam.

Under the irradiation of wavelength >300 nm UV irradiation, >95% selectivity for cyclohexanone was obtained (eq 6), which is quite different from the industrial production of K/A oil by oxidation of cyclohexane with O₂.²⁶ The oxidation of cyclohexane with O₂ mediated by TiO₂ was not governed by a simple uncontrolled autoxidation process. Thus, Scheme 6 was proposed to describe the electron transfer from the substrates to the UV excited TiO₂ and ensuing interaction between the activated substrate with O₂. The e_{cb}⁻ of TiO₂ plays an essential role to prevent the propagation of the organic O-centered free radicals, which renders a high selectivity for

SCHEME 6. Proposed Reaction Mechanism for the Photocatalytic Production of Cyclohexanone over TiO₂ Catalyst

cyclohexanone. Attenuated total reflection Fourier transform infrared (ATR-FTIR) could validate the reaction pathway.²⁷ The increase of the concentration of Ti³⁺ in TiO₂ has a positive effect on the photocatalytic activity and selectivity for ketone. With ¹⁸O₂ as the oxidant, TiO₂ surface bonded ¹⁸O could be observed with ATR-FTIR.²⁸



The oxygen transfer pathway mediated by TiO₂ photocatalysis also tells us that caution should be exercised before concluding the origin of O atoms in the products during oxidation reactions, wherein the incorporation of atmosphere O₂ might be counterintuitively involved in the process for product formation. The oxidation of different substrates such as alcohols, amines, and cyclohexane with O₂ mediated by TiO₂ photocatalysis follows similar oxygen transfer pathways, suggesting the generality of concerted effect of both h_{vb}⁺ and e_{cb}⁻ of TiO₂ to execute an oxidation event under UV irradiation.

3. Aerobic Oxidation of Organic Substrates on TiO₂ under Visible Light Irradiation

Visible light constitutes the majority of energy in solar spectrum, which is more attractive for synthetic purpose. To circumvent the lack of visible light absorption for the

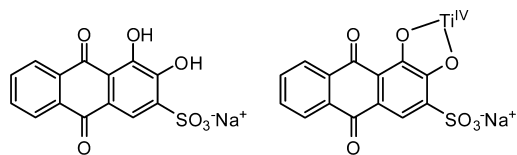


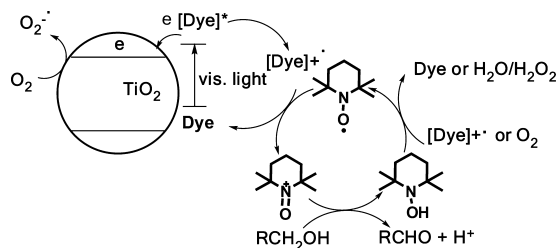
FIGURE 1. Molecular formula of Alizarin Red S (left) and its bidentate chelating adsorption mode on TiO₂ (right).

majority of organic substrates, basically, three strategies could be used to achieve the goal of visible light induced aerobic oxidation on TiO₂: (1) anchoring an organic dye on the surface of TiO₂; (2) forming a visible light absorbing surface complex by complexation of colorless substrates on the surface TiO₂; (3) constructing special antenna by grafting organic molecules on TiO₂ via covalent bonding upon visible light irradiation to induce further oxidation reaction. To this end, we will describe our recent research results on the oxidation of alcohols, amines, and alkanes with O₂ on TiO₂ under visible light irradiation in line with these three different strategies.

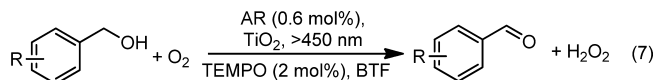
We have previously reported that the organic dyes are susceptible to degradation with O₂ on TiO₂ under visible light irradiation in aqueous solution.²⁹ Anchoring the cationic dye thiazole orange or colorless 2,3-dihydroxynaphthalene on TiO₂ to form a visible light absorbing surface complex could prompt the generation of H₂ or reduction of nitrobenzene with triethanolamine under O₂-free conditions.^{30,31} With O₂ as the oxidant, after the injection of electron from visible light excited dye to the conduction band of TiO₂, dye^{•+} free radicals are generated. The complicated interactions between dye^{•+}, O₂, e_{cb}⁻, and H₂O lead to the degradation of the dye molecules. In order to prevent this degradation reaction, we can carry out the oxidation reactions in an inert organic solvent to exclude the effect of H₂O. Then we can add a suitable electron transfer mediator, which could facilitate the exodus of positive charges of dye^{•+} to substrate molecules in an attempt to prevent their unselective autoxidations while the conduction band of TiO₂ expedites the electron transfer to O₂ to complete the redox processes. Thereby, successful oxidation of alcohols with O₂ under visible light irradiation is achievable if all these factors are orchestrated in an ordered manner.

To meet all these criteria, a successful assembly for the oxidation of alcohols with O₂ exposed to >450 nm visible light irradiation has been constructed in BTF (eq 7).³² Alizarin Red S (AR) was the best sensitizer among those dyes examined to initiate the oxidation reaction which is in part ascribed to its resilience which can be proven by a turnover number of 665 during scale-up reaction, good visible light

SCHEME 7. The Proposed Visible Light Induced Reaction Cycles in the Dye/TiO₂/TEMPO System



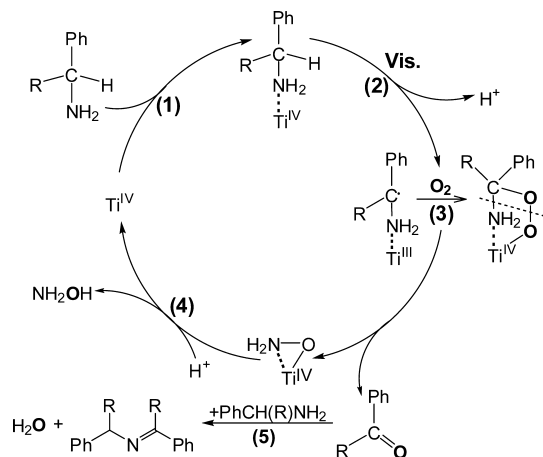
absorption, and superior reversible redox properties as an anthraquinone dye.



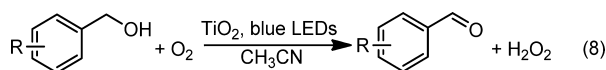
Another factor is the strong bidentate chelating adsorption of this molecule on TiO₂ (Figure 1), which could promote electron transfer from the visible light excited organic dye to the conduction band of TiO₂ and ultimately to O₂. (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) was selected as the electron transfer mediator because it is a well-recognized organocatalyst for selective oxidation of alcohols into corresponding aldehydes or ketones. Moreover, the redox potential of TEMPO matches well with that of the AR^{•+} free radical, which could restore AR^{•+} free radical to its ground state, AR. The proposed reaction mechanism is summarized in Scheme 7. Electron spin resonance (ESR) is a useful tool to probe the surface free radical species. The advent of AR^{•+} on the surface of TiO₂ and its disappearance upon addition of TEMPO were confirmed by ESR spectra in agreement with Scheme 7.³²

This assembly was suitable for the oxidation of benzyl alcohol and its derivatives with O₂ under visible light irradiation with excellent selectivities (97–99%) for corresponding aldehydes at conversions of 49–100%. Allylic and aliphatic alcohols could also be transformed into corresponding aldehydes with selectivities of 93–98% at 20–71% conversions. However, the oxidation of cyclohexanol with O₂ was very sluggish with 10% conversion after 16 h of visible light irradiation due to the low efficiency of TEMPO in mediating the oxidation of secondary alcohols.

In fact, the selective oxidation of alcohols with O₂ could be achieved under irradiation of blue light emitting diodes (LEDs) on the surface of TiO₂ without the assistance of additional dyes (eq 8).³³ The surface complexation between alcohols and anatase TiO₂ could cause the visible light absorption, which further leads to the oxidation of alcohols with O₂ under the irradiation of blue LEDs. Excellent

SCHEME 8. Proposed Mechanism for Visible-Light-Induced Formation of Imines by Oxidation of Amines on Anatase TiO₂

selectivities of >99% were achieved at conversion of 100% for the oxidation of benzyl alcohol and its derivatives with O₂ on anatase TiO₂. We believe that the formation of aldehydes under this condition should follow the same mechanism as in the oxidation of alcohols with O₂ on TiO₂ under UV irradiation (Scheme 2) unlike the mechanism proposed by the authors in line with the traditional mechanism of TiO₂ photocatalysis.

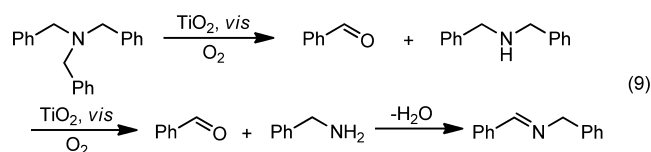


Because amines are stronger complexation substrates than alcohols, we hypothesized that the oxidation of amines with O₂ should work much better under visible light irradiation on TiO₂. Indeed, we observed a red shift of absorption spectra into the visible light range upon the surface complexation between amines and anatase TiO₂. This is a precondition for the oxidation of amines under visible light irradiation. It was discovered that the selective formation of imines could even be achieved on high surface area anatase TiO₂ exposed to >420 nm visible light irradiation with atmospheric O₂.³⁴

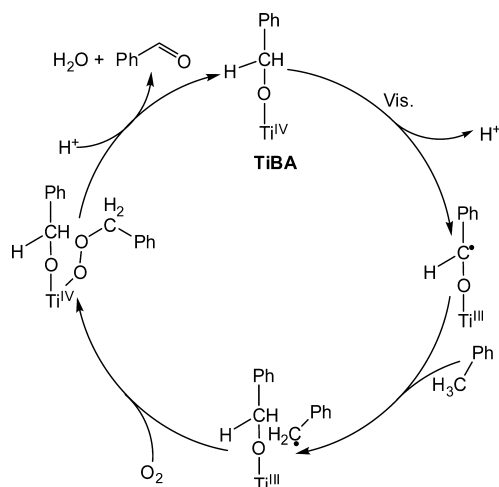
Under this circumstance, without foreign additives such as AR and TEMPO as in the case of oxidation of alcohols, highly selective oxidation of amines with O₂ on anatase TiO₂ exposed to >420 nm irradiation was achieved. The detailed reaction mechanism is summarized in Scheme 8. After surface complexation (step 1), carbon centered surface bound radicals could be generated upon visible light irradiation (step 2). During the oxygen transfer process (step 3), the electrons from substrate are shuttled by the conduction band of TiO₂, meanwhile e_{cb}⁻ prevents the autoxidation of amine in a fashion similar to the selective oxidation of

amines with O₂ on TiO₂ photocatalyst under UV irradiation (Scheme 4). The restoration of the TiO₂ surface will complete the photocatalytic cycle (step 4); the condensation between amine and aldehyde will afford the imine product (step 5). Unlike the oxidation of alcohols, the TiO₂ photocatalyst does not deactivate quickly in the oxidation of amines, which might be ascribed to the easier decomposition of hydroxylamine species than the *side-on* peroxides in Scheme 3.

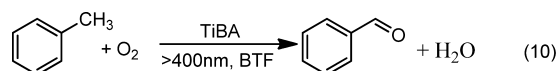
For the oxidation of primary and secondary benzylic amines, the product distribution follows the same pattern as the oxidation of amines on Degussa P25 TiO₂ under UV irradiation (eqs 6 and 7). Selectivities of 70–94% for imines were achieved for the oxidation of benzylamine and its derivatives at conversions of 78–95%; 15–31% selectivities for aldehydes in addition to 40–65% of imines were achieved for the oxidation of dibenzylamine and its derivatives at conversions of 44–81%. Importantly, when tribenzylamine was selected as the substrate, the product distribution was also a result of the oxygen transfer pathway on anatase TiO₂ under visible light irradiation (eq 9). The C–N single bond breaking of tribenzylamine will result in the formation of benzaldehyde and dibenzylamine. The C–N single bond breaking of dibenzylamine and subsequent C=N double bond making via nucleophilic attack of the benzaldehyde by benzylamine afforded the imine. All the proposed intermediates were detected directly in addition to the targeted imine products. Imine (27%), dibenzylamine (24%), and benzaldehyde (39%) were obtained as the products for the oxidation of tribenzylamine on anatase TiO₂ exposed to >420 nm visible light irradiation at 50% conversion.



Inspired by success of the selective oxidation of alcohols and amines with O₂ by TiO₂ photocatalysis under UV and visible light irradiation aforementioned, a new type of photocatalyst was designed for novel aerobic oxidation reactions.³⁵ The photocatalysts were prepared by grafting titanate (H₂Ti₃O₇) in benzyl alcohol solvent in an autoclave at 130 °C for 48 h. The obtained titanate grafting with benzyl alcohol via covalent bonding (Ti^{IV}–O–CH₂–Ph, denoted as TiBA) could work for a more challenging sp³ C–H bond activation of aromatic alkanes. Exposed to >400 nm visible light irradiation, TiBA could be an efficient photocatalyst for

SCHEME 9. Possible Mechanism for the Oxidation of Aromatic Alkane with O₂ on TiBA under Visible Light Irradiation

the oxidation of toluene with O₂ to a selectivity of 94% for benzaldehyde at 8.9% conversion in BTF (eq 10).



Very recently, a dual reaction channel mechanism based on a first-principles continuum solvation method was proposed to explain the interfacial oxygen transfer pathway for the aerobic oxidation of alcohols by TiO₂ photocatalysis.³⁶ However, according to this dimer pathway, TiBA could not act as a photocatalyst for oxidation of toluene with O₂ due to the premature desorption of grafted benzyl alcohol. Thus, the monomer pathway is more plausible to explain the oxidation of toluene by TiBA under visible light irradiation. The possible mechanism is summarized in Scheme 9. The visible light activity of TiBA works in a mechanism similar to the oxidation of amines on the surface of TiO₂, while the covalently bonded benzyl alcohol instead of benzylamine surface complex acted as the antenna molecule to adsorb visible light. Exposed to >400 nm visible light irradiation, the same carbon-centered free radical (TiBA•) for the oxidation of alcohols in Scheme 2 will be generated, acting as a redox-active ligand to induce further oxidation. The interaction of TiBA• and toluene could afford the toluene free radical, which could be captured by O₂, while e_{cb}⁻ plays an essential role to ensure the high selectivity of benzaldehyde. The stability of the obtained photocatalyst was evaluated by the recycle experiments under UV irradiation. The activity decreased significantly at the fourth cycle, ascribed to the adsorption of benzaldehyde, which could be restored partly by sonication.

4. Concluding Remarks

In this Account, we have summarized our and other groups' recent work on the selective oxidation of organic substrates with O₂ mediated by TiO₂ photocatalysis. An oxygen transfer pathway was uncovered during the oxidation event that could help us understand the molecular mechanism for the interfacial reactions on TiO₂. It is traditionally accepted that for a semiconductor photocatalyst such as TiO₂ under the illumination of UV, two photocarriers will be created to carry out their independent reduction and oxidation processes. On the contrary, we find that the concerted effect of h_{vb}⁺ and e_{cb}⁻ contributes directly to the formation of products in the oxidation processes, while the e_{cb}⁻ could play an essential role in the selectivity control over the oxidation products. This mechanism could merit TiO₂ photocatalyst being a good candidate for selective oxidation of organic substrates into the corresponding oxofunctionalized products with O₂ under UV or visible light irradiation. Shape selectivity could also be achieved for redox reactions by atomic layer deposition of a nanoporous Al₂O₃ layer on TiO₂ photocatalyst.³⁷ More versatile and highly selective oxidation of organic substrates with O₂ mediated by metal oxide photocatalysis could be envisioned and implemented in appropriate reaction conditions driven by solar energy to meet the energy and environmental challenges of redox chemical syntheses.

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FOOTNOTES

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