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C–H bond activation of fluorene over a TiO₂ photocatalyst by ligand-to-metal charge transfer under visible light irradiation†

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A novel approach for additive-free oxidation of a C–H bond under mild conditions is proposed. Irradiation of visible light to fluorene in a non-polar solvent in the presence of rutile-type TiO₂ and O₂ induced oxidation of the C–H bond, resulting in the production of fluorenone with a high yield.

Selective oxidation of organic compounds such as alcohols, sulfides, and amines is a key reaction in the chemical industry.^{1–6} Selective oxidation of C–H bonds is a very important reaction for obtaining alcohol and carbonyl compounds (aldehydes, ketones, carboxylic acids, and esters), which are valuable intermediates in the chemical industry, and the reaction has attracted much attention in recent years.⁷ Selective oxidation of these compounds is performed with various stoichiometric oxidizing agents including KMnO₄, MnO₂, CrO₃, and Br₂. Stoichiometric oxidizing agents should be replaced with more environmentally friendly options because they leave behind residues that need to be removed from reaction mixtures. Various efficient heterogeneous catalysts, including metal oxides,^{8,9} metal complexes,^{10,11} nanoparticle catalysts,¹² and microporous/mesoporous materials,^{13,14} have been developed for aerobic oxidative C–H functionalization. However, the reaction generally requires high temperature, high pressure and aggressive oxidants.^{15,16} Therefore, milder catalytic reaction systems for selective oxidation of C–H bonds are favored in terms of green chemistry.

Aiming at the selective oxidation of organic compounds under mild reaction conditions, we have focused on the application of photocatalytic reactions over a semiconductor such as titanium(IV) oxide (TiO₂) for the conversion of organic compounds. Heterogeneous photocatalytic oxidation of organic compounds with oxygen (O₂) molecules has been proposed as

the most plausible method. Only water (H₂O) is formed as the byproduct in these reactions, if the reactions ideally occur. Several research groups have reported selective oxidation of aromatic compounds to carbonyl compounds using a TiO₂ photocatalyst. Palmisano and co-workers¹⁷ demonstrated selective oxidation of benzyl alcohols to the corresponding carbonyl compounds with O₂ in an aqueous solution by band gap excitation of rutile-type TiO₂ under UV irradiation. Different from this photocatalytic reaction, selective oxidation of aromatic alcohols to the corresponding carbonyl compounds over semiconductors under the irradiation of visible light has been reported by several researchers.^{18,19} In their reaction system, alcohols were adsorbed on the surface of TiO₂ and electrons were transferred from the surface complex to TiO₂ under the irradiation of visible light, resulting in the formation of a carbonyl compound and reduction of O₂ molecules. There is interest in this type of photocatalyst that makes it possible to utilize visible light by ligand-to-metal charge transfer²⁰ (LMCT) transition caused by a surface modifier on a photocatalyst. Several reports of photocatalytic oxidation *via* LMCT transition caused by the interaction of catalysts and substrates other than alcohol have been reported.²¹ However, as far as we know, photocatalytic C–H oxidation *via* LMCT transition on TiO₂ has not been reported.

In this study, we examined the visible light-induced aerobic oxidation of fluorene (FLU) to fluorenone (FOne) *via* LMCT transition over TiO₂ as a model reaction of selective C–H oxidation. Here we report (1) the details of photocatalytic oxidation of FLU to FOne under visible light irradiation, (2) the effects of the solvent, reaction temperature and type of TiO₂ on FOne yields, (3) the expandability of this reaction system, and (4) mechanistic insights.

A transmission spectrum of FLU dissolved in hexane indicates that FLU itself did not absorb visible light (Fig. S1(a), ESI†). An emission spectrum of a blue LED and an absorption spectrum of rutile-type TiO₂ are shown in Fig. 1(a). These spectra indicate that oxidation of FLU by photoexcited TiO₂ was negligible. A TEM photograph of TiO₂ indicates that TiO₂ consists of well-crystallized

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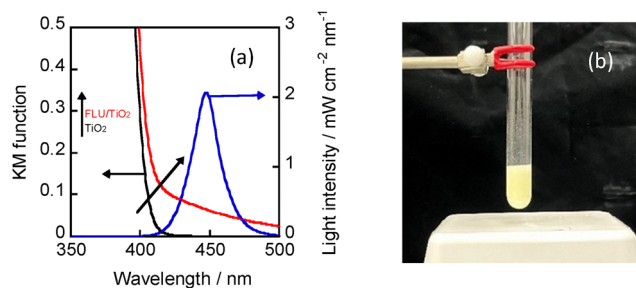


Fig. 1 (a) Absorption spectra of rutile-type TiO₂ (JRC-TiO-3) and FLU/TiO₂ and emission spectrum of visible light irradiated onto the reaction system from a blue LED and (b) a photograph of a suspension of TiO₂ in hexane containing FLU.

particles (Fig. S1(b), ESI[†]). In an SEM photograph of TiO₂ (Fig. S1(c), ESI[†]), secondary particles consisting of fine particles were observed. Fig. 1(b) shows a photograph of a suspension of TiO₂ in hexane containing FLU. The color of the suspension of TiO₂ in hexane without FLU was white (not shown). We noted that the color of the suspension of TiO₂ changed to pale yellow in the presence of FLU in hexane. These results show that coloring of the suspension is caused by the strong interaction of TiO₂ and FLU in hexane, *i.e.*, FLU is adsorbed on the surface of TiO₂, making a surface complex in hexane. The absorption spectrum of the colored TiO₂ recovered from the suspension is also shown in Fig. 1(a), indicating a large overlapping of the absorption of the colored TiO₂ and visible light of the blue LED.

Fig. 2 shows the time courses of the photocatalytic reaction of FLU in a hexane suspension of TiO₂ with irradiation of visible light under O₂. The amount of FLU decreased under light irradiation. Interestingly, FOne was produced after a short induction period (Fig. S2, ESI[†]), indicating that the C–H bond of FLU was activated under the present conditions and O₂ was used as an oxidant for FLU oxidation. The yield of FOne increased with light irradiation and finally reached 83% at 240 min. The material balance (MB) is shown in Fig. 2. The values of MB decreased in the early stage of the reaction, which almost synchronizes the induction period observed in Fig. 2, and after the induction period, the values were almost constant at *ca.* 83% within the experimental errors during the reaction. Fig. 1 and 2 suggest that the oxidation of FLU to FOne under visible light irradiation was induced by light absorption of the surface complex. To confirm this phenomenon, blank reactions were performed (Table S1, ESI[†]) and the results indicated that

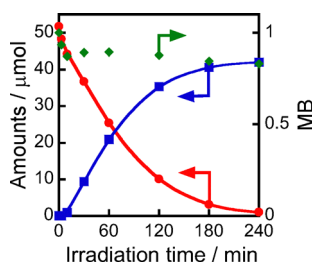


Fig. 2 Time courses of amounts of FLU (●), FOne (■) and MB (◆) in a hexane suspension of TiO₂ under O₂ and irradiation of visible light.

interaction of TiO₂ and FLU, visible light irradiation and O₂ are indispensable for the production of FOne.

To investigate whether the observed reactions are caused by photoabsorption of a surface complex species on TiO₂, photocatalytic reactions were carried out under the irradiation of light having various wavelengths. Fig. S3(a) (ESI[†]) shows the absorption spectrum of the FLU/TiO₂ sample and Fig. S3(b) (ESI[†]) shows an action spectrum of photocatalytic oxidation of FLU over TiO₂. The AQE trend was comparable to the photoabsorption of the FLU/TiO₂ sample, indicating that photoabsorption of the surface complex on TiO₂ is responsible for the oxidation of FLU to FOne over TiO₂ under visible light irradiation.

Photocatalytic oxidation of FLU to FOne was investigated using representative solvents under visible light irradiation, and the yields of FOne after reaction for 4 h are shown in Fig. S4(a) (ESI[†]). Large yields were obtained in the case of hydrocarbons (hexane and octane), while the yields were very small or negligible when acetonitrile and 2-propanol were used. To understand the effects of different solvents on the production of FOne, the amounts of FLU adsorbed on TiO₂ were determined (Fig. S4(b), ESI[†]). The amounts of FLU adsorbed in four solvents showed a tendency similar to that of the FOne yields, and as expected, the yield *vs.* the adsorption amount plot shows a clear correlation between them (Fig. 3(a)). Fig. 3(b) shows the photoabsorption spectra of FLU/TiO₂ samples prepared using four solvents. Interestingly, the photoabsorption properties of the FLU/TiO₂ samples were greatly dependent on the solvents used for the preparation, and the absorption in the visible light region increased in the following order: 2-propanol < acetonitrile < octane < hexane. These results indicate that hydrocarbons cause a strong interaction between TiO₂ and FLU, resulting in photoabsorption in the visible light region. In addition, the absorption spectrum of FLU adsorbed on TiO₂ using each solvent (Fig. 3(b)) showed a similar tendency of photocatalytic activity and FLU adsorbed.

From the adsorption experiments of FOne in hexane, the amount of FOne adsorbed on TiO₂ was roughly estimated to be 16 μmol/200 mg-TiO₂, which is much larger than that of FLU adsorbed on TiO₂ (3.5 μmol/200 mg-TiO₂, Fig. 3(a)). The result indicates a strong interaction between TiO₂ and organic

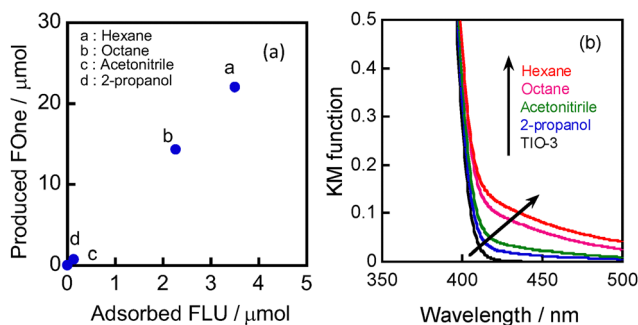


Fig. 3 (a) Correlation between production of FOne and adsorption of FLU on TiO₂, in various solvents and (b) absorption spectra of TiO₂ and FLU/TiO₂ prepared in various solvents.



compounds with an oxygen atom. The short induction period and the decreased material balance observed in Fig. 2 can be explained by the storage of FOne on the surface of TiO₂. The small amount of FLU-TiO₂ complex shows intense photoabsorption in the visible light region, while the FOne adsorbed on TiO₂ does not. The continuous coloration of TiO₂ in the hexane suspension during the photocatalytic reaction means that FOne produced from FLU is gradually desorbed from TiO₂ and diffused into hexane, and then the small amount of new FLU molecule is adsorbed on TiO₂.

Several solvents other than the four solvents stated above were also used for oxidation of FLU under irradiation of visible light and the results are shown in Table S2 (ESI[†]). Saturated hydrocarbons were effective for this reaction and the use of unsaturated hydrocarbons resulted in lower yields. Protic and aprotic polar solvents were not appropriate for this reaction. These results indicate that non-polar hydrocarbons, which do not disturb the interaction between the aromatic ring of FLU and TiO₂, contribute to the formation of the surface complex consisting of TiO₂ and FLU.

Various types of TiO₂ were used for the oxidation of FLU in hexane under visible light irradiation. The yields of FOne after 1 h are shown in Fig. 4 along with their crystalline phases and specific surface areas. Rutile-type TiO₂ exhibited activity for the production of FOne; however, a clear correlation between catalytic performance and specific surface area was not observed. No discernible differences were observed in the XRD patterns of the rutile-type TiO₂ samples (see Fig. S5, ESI[†]). In the case of anatase-type TiO₂, no reaction occurred and the color of TiO₂ remained white. P25 TiO₂, which contains both rutile and anatase phases, exhibited moderate performance. These findings collectively suggest that the presence of rutile-type TiO₂ is a prerequisite for the oxidation of FLU under the condition of visible light irradiation.

A study was conducted to investigate the expandability of C-H oxidation by LMCT transition over TiO₂ under the irradiation of visible light. Various hydrocarbons with similar structures were examined, and the results are presented in Table 1. It was observed that the oxidation of dodecahydrofluorene and cyclopentane, which lack an aromatic ring, did not occur (entries 2 and 3). This finding suggests that an aromatic ring is necessary for C-H oxidation induced by an LMCT transition

Table 1 Results of photocatalytic oxidation of hydrocarbons in hexane suspensions of TiO₂ under the irradiation of visible light^a

Entry	Substrate	Product	Conv./%	Sel./%	MB
1			> 99	83	0.83
2			0	0	> 0.99
3			0	0	> 0.99
4			18	52	0.91
5			0	0	> 0.99

^a Hydrocarbon: 50 μmol, hexane: 5 cm³. TiO₂: JRC-TIO-3, reaction temperature: 45 °C, reaction time: 4 h.

using TiO₂. In the case of indane, which contains a single benzene ring, C-H oxidation occurred (entry 4, Fig. S6, ESI[†]); however, the conversion and selectivity were both lower than those of FLU (entry 1). This suggests that two aromatic rings increase the reactivity of the α carbon. Additionally, the reaction did not proceed when diphenylmethane (DPM) was used as a substrate (entry 5). As shown in Fig. S7(a) (ESI[†]), no adsorption of DPM on TiO₂ was observed. Furthermore, photoabsorption in the visible light range was not observed in the absorption spectrum of DPM/TiO₂ (Fig. S7(b), ESI[†]). It is postulated that the aromatic ring must be adsorbed in a parallel orientation to Ti⁴⁺ for formation of the LMCT complex and photoabsorption of visible light, given that two phenyl groups bound to the sp³ carbon can make a free rotation, thereby making DPM bulky (Fig. S7(c) and (d), ESI[†]).

There have been some reports on the generation of new absorption bands due to LMCT transition from surface complexes on TiO₂ to the CB of TiO₂.²² In addition, the formation of a surface complex species between Ti⁴⁺ (TiO₂) and π electrons (benzene) has been reported.²³ A combination of the findings from this study with those from a previous study leads to the conclusion that the new absorption band is also caused by a surface complex species between Ti⁴⁺ (TiO₂) and π electrons (FLU). Yamamoto *et al.*²³ reported that LMCT occurs in a benzene-TiO₂ system under visible light irradiation and electrons of benzene are injected into the CB of TiO₂, resulting in the formation of benzene cation radicals. A similar mechanism is expected to occur in the FLU-TiO₂ system under visible light, where electrons from FLU are injected into the CB of TiO₂, leading to the formation of FLU cation radicals.

As demonstrated in the blank reactions (Table S1, entry 4, ESI[†]), O₂ plays a pivotal role in the oxidation of FLU, specifically by trapping electrons that are injected into the CB of TiO₂. One-electron reduction of O₂ to superoxide anion radicals (-0.046 V vs. NHE at pH 0) by electrons in the CB of rutile-type TiO₂ (-0.1 V vs. NHE at pH 0) is possible, as indicated by the literature.²⁴ The contribution of these species to the oxidation of FLU will be discussed later.

Scheme 1 shows the stoichiometry of the selective photocatalytic oxidation of FLU to FOne in the presence of oxygen, which indicates that one O₂ molecule is required to produce

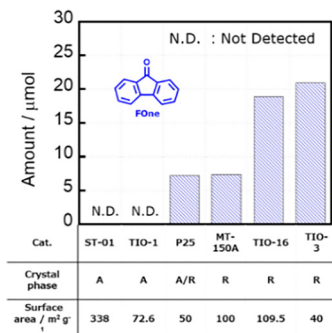
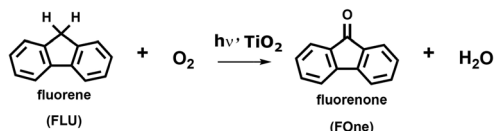


Fig. 4 Effects of various types of TiO₂ on photocatalytic oxidation of FLU to FOne in hexane.





Scheme 1 Photocatalytic oxidation of FLU into FOne over TiO_2 under visible light irradiation.

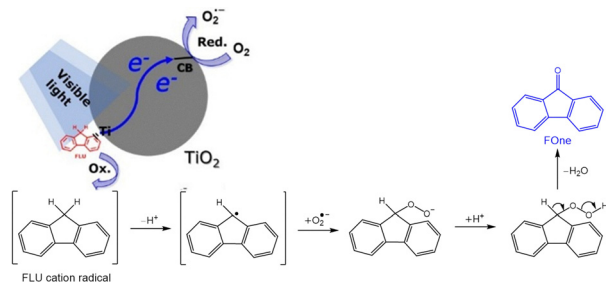


Fig. 5 The expected reaction mechanism of photocatalytic oxidation of FLU to FOne over TiO_2 in the presence of O_2 .

one FOne molecule. In order to confirm the stoichiometry in this reaction, the amount of O_2 in the gas phase was determined together with the production of FOne (Fig. S8, ESI[†]). A linear correlation between them was observed, and the slope of the plot was determined to be 1.01, indicating that selective oxidation of FLU to FOne occurs stoichiometrically and O_2 in the gas phase was only used for the production of FOne.

In consideration of the aforementioned results, the anticipated reaction mechanism of photocatalytic oxidation of FLU to FOne over rutile-type TiO_2 under visible light irradiation is shown in Fig. 5. Initially, electrons of FLU are injected into the CB of TiO_2 through LMCT under visible light irradiation, resulting in the formation of FLU cation radicals and superoxide anion radicals. Subsequent to this, the reaction between the FLU radicals and superoxide anion radicals produces the peroxy anion intermediate, as shown in Fig. 5. Finally, the intermediate is converted into FOne and water.

In conclusion, FLU was adsorbed on rutile-type TiO_2 in hexane and the resultant surface complex species exhibited strong light absorption due to LMCT in the range of visible light. In the presence of O_2 , FLU was converted to FOne with a high yield under visible light irradiation. This reaction has the following advantages compared to previous methods: (1) it proceeds under visible light irradiation, (2) molecular oxygen can be used as the oxidant, (3) no additives are necessary, and (4) no complicated procedures are needed.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.[†]

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