

## Supporting information

# Visible light-induced Minisci reaction through photoexcitation of surface

## Ti-peroxo species

Shimpei Naniwa,<sup>a</sup> Akira Yamamoto<sup>a,b</sup> and Hisao Yoshida<sup>\*a,b</sup>

<sup>a</sup> *Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Yoshida Nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan*

<sup>b</sup> *Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8520, Japan*

\* E-mail address: yoshida.hisao.2a@kyoto-u.ac.jp

## Content

1. Procedure of photodeposition method.....	2
2. State of the reaction mixture .....	2
3. Procedure of iodometry .....	2
4. Optimization of additives .....	2
4.1. Selection of acid additive .....	2
4.2. Composition of the reaction mixture .....	3
5. Optimization of photocatalyst.....	4
5.1. Titanium oxide .....	4
5.2. Loading amount of Pd co-catalyst .....	5
6. Long time reaction with 0.1 wt% Pd-loaded TiO <sub>2</sub> .....	6
7. Reaction tests of quinoline and THF .....	6
References .....	7

## 1. Procedure of photodeposition method

The samples were prepared by a photodeposition method using the TiO<sub>2</sub> powder and an aqueous methanol solution of PdCl<sub>2</sub> (Kishida Chemical, 99%) as follows. The TiO<sub>2</sub> powder (4.0 g) was dispersed in ion-exchanged water (300 ml) and was irradiated with a ceramic xenon lamp (PE300BUV, 300 W) for 30 min. Then, methanol (100 ml) and the desired amount of the metal precursor solution were added to the suspension and the contents were magnetically stirred for 15 min without irradiation, followed by stirring in the light for 1 h. It was then filtered off with suction, washed with ion-exchanged water, and dried at 323 K for 12 h to obtain the metal-loaded TiO<sub>2</sub> photocatalysts.

## 2. State of the reaction mixture



**Fig. S1** Reaction mixture of pyridine, THF, TFA, H<sub>2</sub>O<sub>2</sub>, and the pristine TiO<sub>2</sub> photocatalyst (JRC-TIO-6).

## 3. Procedure of iodometry

H<sub>2</sub>O<sub>2</sub> in reaction solution was quantified by iodometry. The procedure was as follows. 0.2 mL of the reaction solution and 0.5 mL of 1 M sulfuric acid aqueous solution were added to 2.0 mL of potassium iodide aqueous solution (100 g L<sup>-1</sup>), giving a yellow color solution. After 5 minutes, the solution was titrated by 0.01 M sodium thiosulfate solution using starch aqueous solution as an indicator. No color change was confirmed with a solution without H<sub>2</sub>O<sub>2</sub> after adding sulfuric acid and potassium iodide.

## 4. Optimization of additives

### 4.1. Selection of acid additive

It is known that Minisci reaction proceeds through an attack of alkyl radical to a protonated heteroaromatic base in the presence of acid. Thus, property of acid is expected to affect the reaction. In order to select the most suitable acid for the present system, reaction tests were carried out under visible light with various acids (Table S1). Five organic acids which have different acidity were used: trifluoroacetic acid (TFA), tetrabromoacetic acid (TBA), difluoroacetic acid (DFA), acetic acid (AcOH), and trifluoroethanol (TFE). Among them, TFA gave the highest TPs yield (Table S1, entry 1). Other organic acids (Table S1, entries 2–5) were active only for OTs production and the largest amount of OTs was produced with TBA (Table S1, entry 2). Since trace amount of brominated products such as bromopyridine were detected, TBA would be activated during the reaction. Inorganic acid such as H<sub>2</sub>SO<sub>4</sub> was also examined (Table S1, entry 6). The reaction also afforded TPs but with much smaller amount than that with TFA (Table S1, entry 1). Based on these results, TFA was chosen as an acid in the following reaction tests.

**Table S1** Results of reaction tests performed with different acid<sup>a</sup>

Entry	Acid <sup>b</sup>	pK <sub>a</sub> <sup>c</sup>	Products <sup>d</sup> / μmol		Yield of TPs <sup>e</sup> (%)	Selectivity <sup>f</sup> (%)	
			TPs	OTs		S <sub>py</sub>	S <sub>THF</sub>
1	TFA	0.23	15	40	7.6	>99	27
2	TBA	0.22	n.d. <sup>g</sup>	183	0	0	0
3	DFA	1.3	0.18	25	0.092	>99	0.64
4	AcOH	4.8	n.d. <sup>g</sup>	31	0	0	0
5	TFE	12	n.d. <sup>g</sup>	35	0	0	0
6 <sup>h</sup>	H <sub>2</sub> SO <sub>4</sub>	-3	0.36	13	0.18	>99	2.7

<sup>a</sup> Reaction conditions: pyridine (0.2 mmol), THF (24 mmol), 30 % H<sub>2</sub>O<sub>2</sub> aq. (22.5 μL, 0.2 mmol of H<sub>2</sub>O<sub>2</sub>), and acid (0.2 mmol) with the 0.1 wt% Pd-loaded TiO<sub>2</sub> photocatalyst (JRC-TIO-6) were used, irradiation wavelength was 400 ± 10 nm, the light intensity was 9 mW cm<sup>-2</sup> measured at 415 ± 55 nm in wavelength, and the reaction time was 1 h. <sup>b</sup> Organic acid used in the reaction test. TFA, TBA, DFA, AcOH, and TFE are trifluoroacetic acid, tribromoacetic acid, difluoroacetic acid, acetic acid, and trifluoroethanol, respectively. <sup>c</sup> pK<sub>a</sub> in water at 25 °C. <sup>d,e,f</sup> See the caption in Table 1 in the main text. <sup>g</sup> Not detected. <sup>h</sup> 0.2 mL of 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution was added.

#### 4.2. Composition of the reaction mixture

The amounts of H<sub>2</sub>O<sub>2</sub> and TFA were optimized in the reaction using the Pd(0.1)/TiO<sub>2</sub> sample under visible light (400 ± 10 nm in wavelength).

The amount of H<sub>2</sub>O<sub>2</sub> was first optimized with 0.2 mmol of TFA (Table S2). When the reaction tests were carried out without H<sub>2</sub>O<sub>2</sub> (Table S2, entry 1), the reaction slightly proceeded to produce 0.71 μmol of TPs and 0.41 μmol of OTs with 61% selectivity based on THF (S<sub>THF</sub>). The reaction in this case would proceed by the excitation of TiO<sub>2</sub> since rutile TiO<sub>2</sub> can absorb visible light around 400 nm in wavelength. The addition of H<sub>2</sub>O<sub>2</sub> up to 0.2 mmol (Table S2, entries 2–4) drastically promoted the reaction while it decreased S<sub>THF</sub>. Further increase of H<sub>2</sub>O<sub>2</sub> (Table S2, entries 5 and 6) inhibited TPs production and promoted OTs production, indicating that too high concentration of hydroxyl radical promotes reaction between THF radical and hydroxyl radical predominantly. Therefore, 0.2 mmol was found to be the optimum amount of H<sub>2</sub>O<sub>2</sub>.

Next, the amount of TFA was optimized with 0.2 mmol of H<sub>2</sub>O<sub>2</sub> (Table S3). The reaction without TFA (

Table S3, entry 1) gave only OTs. The yield of TPs increased with increasing the amount of TFA (

Table S3, entries 2–4) and reached a plateau with more than 0.2 mmol addition of TFA (Table S3, entries 5 and 6). Therefore, 0.2 mmol was found to be the optimum amount of TFA.

**Table S2** Results of reaction tests performed with different amount of H<sub>2</sub>O<sub>2</sub><sup>a</sup>

Entry	H <sub>2</sub> O <sub>2</sub> / mmol	Products <sup>b</sup> / μmol		Yield of TPs <sup>c</sup> (%)	Selectivity <sup>d</sup> (%)	
		TPs	OTs		S <sub>py</sub>	S <sub>THF</sub>
1	0.00	0.71	0.41	0.36	>99	61
2	0.018	5.1	4.0	2.6	>99	54
3	0.089	12	30	6.1	>99	28
4	0.2	15	39	7.6	>99	28
5	0.4	4.4	68	2.2	>99	5.6
6	0.8	0.40	80	0.20	>99	0.49

<sup>a</sup> Reaction conditions: pyridine (0.2 mmol), THF (24 mmol), 30 % H<sub>2</sub>O<sub>2</sub> aq., and TFA (0.2 mmol) with the 0.1 wt% Pd-loaded TiO<sub>2</sub> photocatalyst (JRC-TIO-6) were used, irradiation wavelength was 400 ± 10 nm, the light intensity was 9 mW cm<sup>-2</sup> measured at 415 ± 55 nm in wavelength, and reaction time was 1 h. <sup>b,c,d</sup> See the caption in Table 1 in the main text.

**Table S3** Results of reaction tests performed with different amount of TFA<sup>a</sup>

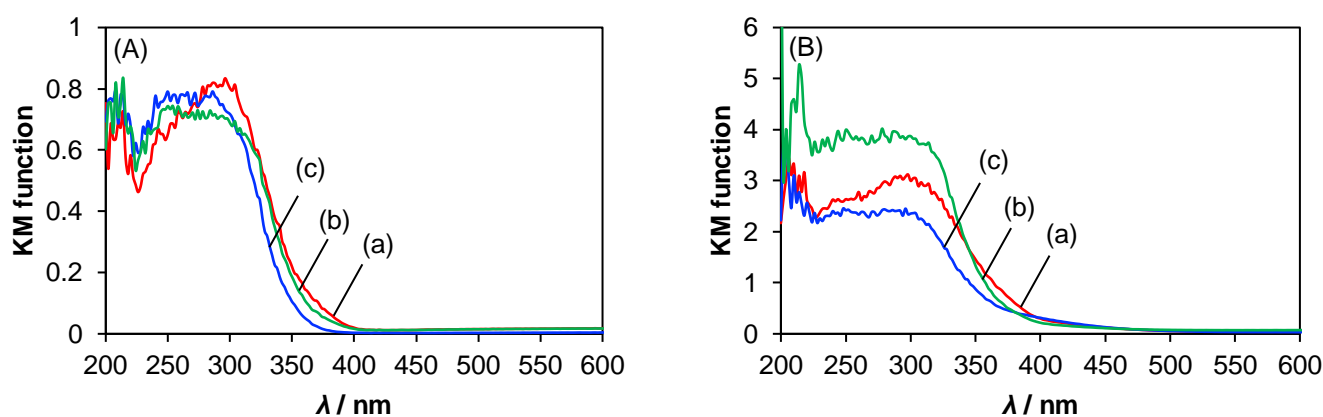
Entry	TFA / mmol	Products <sup>b</sup> / $\mu\text{mol}$		Yield of TPs <sup>c</sup> (%)	Selectivity <sup>d</sup> (%)	
		TPs	OTs		$S_{\text{py}}$	$S_{\text{THF}}$
1	0.00	n.d. <sup>e</sup>	33	0	0	0
2	0.052	3.5	39	1.8	>99	8.2
3	0.1	7.2	22	3.6	>99	24
4	0.2	15	40	7.6	>99	27
5	0.4	14	38	7.1	>99	27
6	0.8	13	31	6.3	>99	28

<sup>a</sup> Reaction conditions: pyridine (0.2 mmol), THF (24 mmol), 30 % H<sub>2</sub>O<sub>2</sub> aq. (22.5  $\mu\text{L}$ , 0.2 mmol of H<sub>2</sub>O<sub>2</sub>), and TFA with the 0.1 wt% Pd-loaded TiO<sub>2</sub> photocatalyst (JRC-TIO-6) were used, irradiation wavelength was  $400 \pm 10$  nm, the light intensity was  $9 \text{ mW cm}^{-2}$  was measured at  $415 \pm 55$  nm in wavelength, and reaction time was 1 h. <sup>b,c,d</sup> See the caption in Table 1 in the main text. <sup>e</sup> Not detected.

## 5. Optimization of photocatalyst

### 5.1. Titanium oxide

First, UV-vis spectra of TiO<sub>2</sub> samples of different crystal phase were recorded in a diffuse reflectance (RD) mode (Fig. S2). Three TiO<sub>2</sub> samples were used such as JRC-TIO-6 (rutile phase,  $100 \text{ m}^2 \text{ g}^{-1}$ ), JRC-TIO-4 (a mixture of rutile and anatase phases,  $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ ), and JRC-TIO-14 (anatase phase,  $338 \text{ m}^2 \text{ g}^{-1}$ ). Fig. S2A shows DR UV vis spectra of these samples diluted by BaSO<sub>4</sub>, and Fig. S2B shows spectra of the samples adsorbed with H<sub>2</sub>O<sub>2</sub>. After H<sub>2</sub>O<sub>2</sub> adsorption, all of the samples extended its light absorption range to around 500 nm in wavelength (Fig. S2B), which should be due to the formation of the surface Ti-peroxo species. The color of these samples with H<sub>2</sub>O<sub>2</sub> were yellow.



**Fig. S2** (A) DR UV-vis spectra of different TiO<sub>2</sub> samples diluted by BaSO<sub>4</sub>, (a) the rutile sample (JRC-TIO-6), (b) the mixture sample (JRC-TIO-4), and (c) the anatase sample (JRC-TIO-14). (B) DR UV-vis spectra of different TiO<sub>2</sub> sample adsorbed with H<sub>2</sub>O<sub>2</sub>. 50  $\mu\text{L}$  of 30 % H<sub>2</sub>O<sub>2</sub> aqueous solution was added to the samples.

Next, reaction tests were carried out using the TiO<sub>2</sub> samples loaded with 0.1 wt% Pd (Table S4). When the reaction tests were carried out under visible light (Table S4, entries 1–3), 15 μmol of TPs (sum of isomers of tetrahydrofuranlypyridine) and 40 μmol of OTs (sum of oxidized products of THF) were obtained with the rutile sample (Table S4, entry 1). The mixture sample showed lower activity than the rutile sample (Table S4, entry 2). The anatase sample (Table S4, entry 3) gave very small amount of TPs and 39 μmol of OTs. Under UV light (Table S4, entries 4–6), 2.3 μmol of TPs and 16 μmol of OTs were obtained with the rutile sample (Table S4, entry 4).  $S_{\text{THF}}$  was 12 %, which is lower than that under visible light (27 %, Table S4, entry 1).  $S_{\text{THF}}$  with the mixture sample under UV light (27 %, Table S4, entry 5) was similar to that under visible light (30%, Table S4, entry 2). The anatase sample was still inactive for the production of TPs even under UV light (Table S4, entry 6). It is reported that the addition of H<sub>2</sub>O<sub>2</sub> enhances the photocatalytic formation of hydroxyl radical for rutile TiO<sub>2</sub> but inhibits for anatase TiO<sub>2</sub>.<sup>S1</sup> Therefore, in the presence of H<sub>2</sub>O<sub>2</sub>, the rutile sample efficiently produces hydroxyl radical, which would be the active species in the present system as indicated by the scavenging tests (Tables 2 and 3 in the main text), and thus shows much better activity than the anatase sample. Based on the result, the rutile sample was chosen as the best TiO<sub>2</sub> photocatalyst in the following experiments.

**Table S4** Results of reaction tests using photocatalyst of different TiO<sub>2</sub> crystal phase<sup>a</sup>

Entry	$\lambda$ / nm	TiO <sub>2</sub>	Crystal phase	Specific surface area / m <sup>2</sup> g <sup>-1</sup>	Products <sup>b</sup> / μmol		Yield of TPs <sup>c</sup> (%)	Selectivity <sup>d</sup> (%)	
					TPs	OTs		$S_{\text{py}}$	$S_{\text{THF}}$
1	400	JRC-TIO-6	rutile	100	15	40	7.6	>99	27
2	400	JRC-TIO-4	anatase+rutile	50 ± 15	9.1	19	4.6	>99	30
3	400	JRC-TIO-14	anatase	338	0.095	39	0.048	>99	0.24
4	360	JRC-TIO-6	rutile	100	2.3	16	1.1	>99	12
5	360	JRC-TIO-4	anatase+rutile	50 ± 15	3.6	9.3	1.8	>99	27
6	360	JRC-TIO-14	anatase	338	0.13	19	0.066	>99	0.65

<sup>a</sup> Reaction conditions: pyridine (0.2 mmol), THF (24 mmol), 30 % H<sub>2</sub>O<sub>2</sub> aq. (22.5 μL, 0.2 mmol of H<sub>2</sub>O<sub>2</sub>), and TFA (0.2 mmol) with the 0.1 wt% Pd-loaded TiO<sub>2</sub> photocatalyst were used, the light intensity was 9 mW cm<sup>-2</sup> was measured at 415 ± 55 nm in wavelength, and the reaction time was 1 h. <sup>b,c,d</sup> See the caption in Table 1 in the main text.

## 5.2. Loading amount of Pd co-catalyst

Reaction tests were carried out using the rutile TiO<sub>2</sub> photocatalyst loaded with various amount of Pd co-catalyst to optimize the Pd loading amount under visible light (Table S5). The yield of TPs and OTs increased with increasing Pd loading amount from 0 to 0.1 wt% (Table S5, entries 1–3). However, the yield of TPs decreased with further increasing loading amount than 0.1 wt% while that of OTs kept increasing (Table S5, entries 4 and 5). Based on these results, the 0.1 wt% Pd loaded rutile TiO<sub>2</sub> sample (Pd(0.1)/TiO<sub>2</sub>) was employed as the best metal loaded photocatalyst.

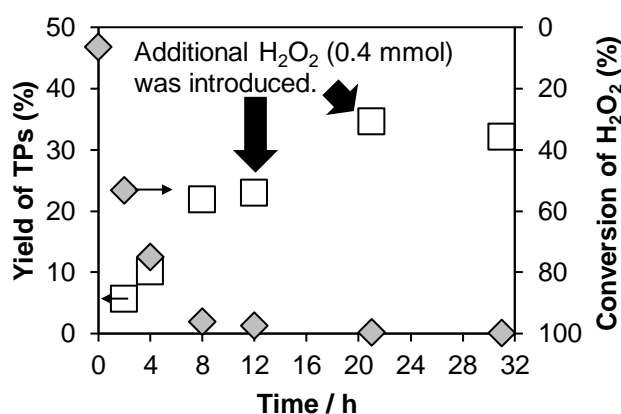
**Table S5** Results of reaction tests using photocatalyst with different loading amount of Pd cocatalyst<sup>a</sup>

Entry	wt% of Pd	Products <sup>b</sup> / $\mu\text{mol}$		Yield of TPs <sup>c</sup> (%)	Selectivity <sup>d</sup> (%)	
		TPs	OTs		$S_{\text{PY}}$	$S_{\text{THF}}$
1	0	8.6	15	4.6	>99	39
2	0.05	11	31	7.0	>99	26
3	0.1	15	40	7.6	>99	27
4	0.2	4.9	82	2.5	>99	5.5
5	0.5	2.1	90	1.1	>99	2.3

<sup>a</sup> Reaction conditions: pyridine (0.2 mmol), THF (24 mmol), 30 %  $\text{H}_2\text{O}_2$  aq. (22.5  $\mu\text{L}$ , 0.2 mmol of  $\text{H}_2\text{O}_2$ ), and TFA (0.2 mmol) with the Pd-loaded  $\text{TiO}_2$  photocatalyst (JRC-TIO-6) were used, irradiation wavelength was  $400 \pm 10$  nm, the light intensity was  $9 \text{ mW cm}^{-2}$  was measured at  $415 \pm 55$  nm in wavelength, and the reaction time was 1 h. <sup>b,c,d</sup> See the caption in Table 1 in the main text.

## 6. Long time reaction with 0.1 wt% Pd-loaded $\text{TiO}_2$

Long time reaction test was carried out using the Pd loaded sample (Fig. S3). The reaction was stopped after 8 h as with that using the pristine sample while the yield of TPs was higher than that with the pristine sample such as 22 %. The addition of  $\text{H}_2\text{O}_2$  after 12 h resumed the reaction and the yield reached 35 % after 21 h. However, further addition of  $\text{H}_2\text{O}_2$  after 21 h did not improve the yield but promoted successive reactions to give several bifunctionalized pyridines with two THF molecules.



**Fig. S3** Time course of the Minisci reaction between pyridine and THF using the 0.1 wt% Pd-loaded  $\text{TiO}_2$  photocatalyst (JRC-TIO-6). Pyridine (0.4 mmol), THF (48 mmol), 30 %  $\text{H}_2\text{O}_2$  aq. (45  $\mu\text{L}$ , 0.4 mmol of  $\text{H}_2\text{O}_2$ ), and TFA (0.4 mmol) were used. Additional  $\text{H}_2\text{O}_2$  (0.4 mmol) was introduced after 12 h and 21 h.

## 7. Reaction tests of quinoline and THF

Reaction tests were carried out using quinoline instead of pyridine to investigate the generality of the present system (Table S6). The reaction afforded mainly two isomers of tetrahydrofurylquinoline (TQs) in a ratio of 3 : 2. The selectivities were almost same between the reaction under UV light (Table S6, entry 1) and visible light (Table S6, entry 2). The yield in 2 h was 14 % under UV light and 20 % yield under visible light, which is much higher than that of the reaction with pyridine (Table 1, entries 1 and 2 in the main text).

**Table S6** Results of reaction tests of quinoline and THF<sup>a</sup>

Entry	$\lambda$ / nm	Products <sup>b</sup> / $\mu\text{mol}$		Yield of TQs <sup>c</sup> (%)	Selectivity <sup>d</sup> (%)	
		TQs	OTs		$S_{\text{quino}}$	$S_{\text{THF}}$
1	360	28	1.2	14	>99	84
2	400	39	1.4	20	>99	87

<sup>a</sup> Reaction conditions: quinoline (0.2 mmol), THF (24 mmol), 30 % H<sub>2</sub>O<sub>2</sub> aq. (22.5  $\mu\text{L}$ , 0.2 mmol of H<sub>2</sub>O<sub>2</sub>), and TFA (0.2 mmol) with the 0.1 wt% Pd-loaded TiO<sub>2</sub> photocatalyst were used, and the reaction time was 2 h. <sup>b</sup> TQs: total amount of tetrahydrofurylquinoline. OTs: total amount of 2-hydroxytetrahydrofuran,  $\gamma$ -butyrolactone, and  $\alpha$ -hydroxy- $\gamma$ -butyrolactone. <sup>c</sup> Yield of TQs based on the introduced quinoline. <sup>d</sup> Selectivity to TQs. The selectivity based on pyridine was calculated as  $S_{\text{quino}} = [100 \times \text{TQs} (\mu\text{mol})] / [(\text{TQs} + \text{byproducts from quinoline}) (\mu\text{mol})]$ ; the selectivity based on THF was calculated as  $S_{\text{THF}} = [100 \times \text{TPs} (\mu\text{mol})] / [(\text{TPs} + \text{OTs}) (\mu\text{mol})]$ .

## References

- S1 T. Hirakawa, K. Yawata and Y. Nosaka, *Appl. Catal. A Gen.*, 2007, **325**, 105.