

## Article

# Selective Hydrogen Peroxide Formation by Titanium Dioxide Photocatalysis with Benzylic Alcohols and Molecular Oxygen in Water

Yasuhiro Shiraishi, Shunsuke Kanazawa, Daijiro Tsukamoto, Akimitsu Shiro, Yoshitsune Sugano, and Takayuki Hirai

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/cs400511q • Publication Date (Web): 23 Aug 2013

Downloaded from http://pubs.acs.org on August 27, 2013

## **Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties. 1

# Selective Hydrogen Peroxide Formation by Titanium Dioxide Photocatalysis with Benzylic Alcohols and Molecular Oxygen in Water

Yasuhiro Shiraishi,\* Shunsuke Kanazawa, Daijiro Tsukamoto, Akimitsu Shiro, Yoshitsune Sugano, and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

Supporting Information Placeholder

KEYWORDS: Photocatalysis; Hydrogen peroxide; Titanium dioxide; Peroxide; Surface chemistry

**ABSTRACT:** Photocatalytic production of hydrogen peroxide ( $H_2O_2$ ) on semiconductor catalysts with alcohol as a hydrogen source and molecular oxygen ( $O_2$ ) as an oxygen source has attracted much attention as a potential method for safe  $H_2O_2$  synthesis, because the reaction can be carried out without the use of explosive  $H_2/O_2$  mixed gases. Early-reported photocatalytic systems with aliphatic alcohol as a hydrogen source, however, produce only a few millimolar levels of  $H_2O_2$ . We found that benzylic alcohols, when used as a hydrogen source for photoreaction in water with titanium dioxide (TiO<sub>2</sub>) photocatalyst, produces very high concentration of  $H_2O_2$  (ca. 40 mM). Raman spectroscopy and electron spin resonance analysis revealed that the enhanced  $H_2O_2$  formation is due to the efficient formation of side-on coordinated peroxo species on the photoactivated TiO<sub>2</sub> surface, via the reaction of benzylic alcohol and  $O_2$ . The peroxo species is readily transformed to  $H_2O_2$ , thus facilitating highly efficient  $H_2O_2$  production.

#### INTRODUCTION

Hydrogen peroxide ( $H_2O_2$ ) is a clean oxidant that emits only water as a byproduct and is widely used in industry for organic synthesis, pulp bleaching, wastewater treatment, and disinfection.<sup>1</sup>  $H_2O_2$  is commercially produced by the anthraquinone method, which has some non-green features such as high energy utilization because of the multistep hydrogenation and oxidation reactions. Recently,  $H_2O_2$  production with  $H_2$  and  $O_2$  gases has been studied extensively with  $Pd^{2-4}$  or Au–Pd bimetallic nanoparticle catalysts.<sup>5–7</sup> This direct synthesis is potentially an alternative process for  $H_2O_2$  production from the viewpoint of green and sustainable chemistry, but some care is necessary for operation because of the potentially explosive nature of  $H_2/O_2$ gas mixtures.

Photocatalytic production of  $H_2O_2$  with semiconductor titanium dioxide (TiO<sub>2</sub>) has also attracted much attention.<sup>8–11</sup> The reaction is usually carried out by UV irradiation of TiO<sub>2</sub> suspended in an O<sub>2</sub>-saturated water with alcohol as electron and proton donor. Photoexcitation of TiO<sub>2</sub> produces electron (e<sup>-</sup>) and positive hole (h<sup>+</sup>) pairs. The h<sup>+</sup> oxidizes alcohol and produces aldehyde and protons.

$$R-CH_2OH + 2h^+ \rightarrow R-CHO + 2H^+$$
(1)

The  $e^-$  on the TiO<sub>2</sub> surface (surface Ti<sup>3+</sup> site) reduces O<sub>2</sub> and produces a superoxo radical.<sup>12</sup>

$$\mathrm{Ti}^{3+}(\mathrm{e}^{-}) + \mathrm{O}_{2} \to \mathrm{Ti}^{4+} - \mathrm{O} - \mathrm{O}^{\bullet}$$
(2)

The superoxo radical is transformed to a hydroperoxo species via further reduction with  $e^-$ . Protonation of the species produces  $H_2O_2$ .<sup>13,14</sup>

$$Ti^{3+}(e^{-}) - O - O^{\bullet} + H^{+} \rightarrow Ti^{4+} - O - OH$$
(3)

$$Ti^{4+} - O - OH + H^{+} \rightarrow Ti^{4+} + H_2O_2$$
 (4)

These reactions proceed at atmospheric pressure and room temperature without H<sub>2</sub> gas and can be a clean and safe H<sub>2</sub>O<sub>2</sub> synthesis. The amount of H<sub>2</sub>O<sub>2</sub> produced, however, is very low (<0.2 mM).<sup>8–11</sup> Several kinds of TiO<sub>2</sub> catalysts modified with fluoride,<sup>15</sup> or loaded with Au<sup>16</sup> or Au–Ag alloy nanoparticles<sup>17</sup> have been proposed so far; however, all of these systems still produce only a few millimolar levels of H<sub>2</sub>O<sub>2</sub>. The low efficiency for H<sub>2</sub>O<sub>2</sub> production on the photoactivated TiO<sub>2</sub> surface is because the hydroperoxo species is very unstable and is easily decomposed by further reduction with e<sup>-</sup> to inactive hydroxide anion.<sup>12</sup>

$$Ti^{3+}(e^{-}) - O - OH + H^{+} \rightarrow Ti^{4+} - {}^{\bullet}OH + OH^{-}$$
(5)

$$Ti^{3+}(e^{-}) \stackrel{\bullet}{\longrightarrow} OH \rightarrow Ti^{4+} + OH^{-}$$
(6)

A new approach is therefore necessary for efficient production of  $\rm H_2O_2$  by photocatalysis.

All of the early-reported systems for photocatalytic  $H_2O_2$  production have employed aliphatic alcohols (e.g. ethanol) as the electron and proton donor.<sup>8–11,15–17</sup> Herein, we report that benzylic alcohols, when used for photoreaction in water with TiO<sub>2</sub> and O<sub>2</sub>, efficiently promote  $H_2O_2$  formation. This photocatalytic system produces very high concentration of  $H_2O_2$  (ca. 40 mM), which is the highest concentration among the early reported systems.<sup>8–11,15–17</sup> Raman spectroscopy and electron spin resonance (ESR) analysis revealed that the enhanced  $H_2O_2$  formation is because photoexcitation of TiO<sub>2</sub> in water with benzylic alcohols and O<sub>2</sub> selectively produces *side-on coordinated peroxo species* on the TiO<sub>2</sub> surface. This peroxo species is readily transformed to  $H_2O_2$ , resulting in efficient  $H_2O_2$  production.

## RESULTS AND DISCUSSION

Photocatalytic Activity for H<sub>2</sub>O<sub>2</sub> Production. Photocatalytic reactions were carried out as follows: water (5 mL) containing TiO<sub>2</sub> (50 mg) and each respective alcohol (350 mM) was photoirradiated with magnetic stirring by a high-pressure Hg lamp ( $\lambda$  >280 nm) with O<sub>2</sub> (1 atm) at 298 K. Anatase TiO<sub>2</sub> (JRC-TIO-1; BET surface area, 73 m<sup>2</sup> g<sup>-1</sup>; average particle size, 21 nm), kindly supplied from Catalyst Society of Japan, was used as a catalyst. Table 1 summarizes the results obtained by 12 h photoreaction. With ethanol (entry 1), the H<sub>2</sub>O<sub>2</sub> concentration is 0.3 mM and the selectivity for H<sub>2</sub>O<sub>2</sub> formation relative to the amount of alcohol consumed (= [H<sub>2</sub>O<sub>2</sub> formed] / [alcohol consumed]  $\times$  100) is only 0.4%. Other aliphatic alcohols are also ineffective for  $H_2O_2$  formation (entries 2-4). In contrast, as shown by entry 5, photoreaction with benzyl alcohol exhibits very high H2O2 selectivity (33%) and produces significantly high concentration of H<sub>2</sub>O<sub>2</sub> (40 mM), which is the highest value among the photocatalytic systems reported earlier.  $\overset{8-11,15-17}{\bullet}$ 

Figure 1 shows the time-dependent change in the amounts of substrate and products during photoirradiation of TiO2 with alcohol and O2 in water. In the case with benzyl alcohol (Figure 1a), the selectivity for  $\mathrm{H_2O_2}$  formation is almost unchanged (>30%) even after prolonged photoirradiation (~30 h), although the rate of H2O2 formation decreases with photoirradiation time due to the subsequent decomposition of  $H_2O_2$  by UV irradiation.<sup>18</sup> In contrast, as shown in Figure 1b, photoreaction with ethanol always shows much lower  $H_2O_2$  selectivity ( $\leq 0.7\%$ ). As shown by entries 6 and 7 (Table 1), substituted benzylic alcohols are also effective for H<sub>2</sub>O<sub>2</sub> production. In addition, the apparent quantum yield for H2O2 formation during photoreaction with benzyl alcohol ( $\Phi_{AOY}$  (%) = [H<sub>2</sub>O<sub>2</sub> formed × 2] / [photon number entering into the reaction vessel] × 100), determined with a 334 nm monochromatic light as a light source, is 29.1%, whereas the  $\Phi_{AQY}$  obtained during photoreaction with ethanol is only 0.5%. These findings clearly suggest that benzylic alcohols are indeed effective for efficient and selective H<sub>2</sub>O<sub>2</sub> production.

As reported,<sup>19</sup> benzylic alcohols are strongly adsorbed onto the TiO<sub>2</sub> surface, and visible light excitation of the formed charge-transferred complex promotes oxidation of alcohols. However, as shown in Table 1 (entry 8), reaction with benzyl alcohol and O<sub>2</sub> on TiO<sub>2</sub> under visible light irradiation (>420 nm) produces very small amount of H<sub>2</sub>O<sub>2</sub>, and the selectivity for H<sub>2</sub>O<sub>2</sub> formation (25%) is lower than that obtained under UV irradiation (33%, entry 5). This suggests that band gap photoexcitation of TiO<sub>2</sub> promotes efficient and selective formation of H<sub>2</sub>O<sub>2</sub>.

Table 1. Results for Photocatalytic H<sub>2</sub>O<sub>2</sub> Production on TiO<sub>2</sub> under Various Conditions<sup>a</sup>

	alcohol	solvent	alcohol consumed	aldehyde or	$H_2O_2$	H <sub>2</sub> O <sub>2</sub> selectivity
entry			$/ \mu mol^{b}$	ketone / $\mu$ mol $^{b}$	/ mM °	/ % <sup>d</sup>
1	ethanol	water	358.0	154.6	0.3	0.4
2	1-propanol	water	340.4	204.9	0.4	0.7
3	1-hexanol	water	453.4	123.5	0.3	0.3
4	2-phenylethanol	water	771.4	257.2	8.4	5.4
5	benzyl alcohol	water	604.1	198.1	39.6	32.8
6	<i>p</i> -nitrobenzyl alcohol	water	587.9	518.5	33.1	28.2
7	1-phenylethanol	water	628.8	397.4	40.2	32.0
8 °	benzyl alcohol	water	85.5	53.0	4.3	25.1
9 <sup>f</sup>	benzaldehyde	water	1311.2 <sup>g</sup>		8.6	
10	benzyl alcohol	CH <sub>3</sub> CN/water (3/7 v/v)	483.6	278.3	26.1	27.0
11	benzyl alcohol	CH <sub>3</sub> CN/water (7/3 v/v)	562.1	305.6	26.7	23.8
12	benzyl alcohol	CH <sub>3</sub> CN	1284.8	673.6	21.1	8.2
13	benzyl alcohol	DMF	420.1	123.3	1.6	1.9
14	benzyl alcohol	benzotrifluoride (BTF)	1163.5	554.9	1.8	0.8

<sup>*a*</sup> Reaction conditions: solvent (5 mL), alcohol (350 mM), catalyst (50 mg), O<sub>2</sub> (1 atm),  $\lambda > 280$  nm (light intensity at 280-400 nm, 13.8 mW cm<sup>-2</sup>), photoirradiation time (12 h). <sup>*b*</sup> Determined by GC. <sup>*c*</sup> Determined by redox titration with KMnO<sub>4</sub> (detection limit: 0.05 mM). <sup>*d*</sup> = [H<sub>2</sub>O<sub>2</sub> formed (µmol)] / [alcohol consumed (µmol)] × 100. <sup>*c*</sup> Photoreaction was carried out under irradiation of visible light ( $\lambda > 420$  nm). <sup>*f*</sup> Benzaldehyde (350 mM) was used as a starting material in place of alcohol. <sup>*s*</sup> The amount of benzaldehyde consumed.

### **ACS Catalysis**





**Figure 1.** Time-dependent change in (bottom) the amounts of substrates and products and (top)  $H_2O_2$  selectivity and carbon balance, during photoirradiation of  $TiO_2$  in water with  $O_2$  and (a) benzyl alcohol or (b) ethanol. Reaction conditions are identical to those in Table 1. The carbon balance for (a) was calculated using the equation, C balance (%) = [benzaldehyde + benzoic acid + ( $CO_2$ )/7] / [benzyl alcohol consumed] × 100. The carbon balance for (b) was calculated using the equation, C balance (%) = [acetaldehyde + acetic acid + ( $CO_2$ )/2] / [ethanol consumed] × 100.





It is also noted that anatase  $TiO_2$  is effective for this reaction, as is observed for common photocatalytic reactions.<sup>20</sup> As shown in Table S1 (Supporting Information), rutile or Degussa P25  $TiO_2$  [a mixture of anatase/rutile particles (ca. 80/20 wt/wt)],<sup>21,22</sup> produces lower amount of  $H_2O_2$  than anatase, although the  $H_2O_2$  selectivities are similar.

As shown in Figure 1a, photocatalytic reaction with benzyl alcohol produces benzaldehyde. This is decomposed by subsequent photocatalytic reaction and is finally converted to  $CO_2$  (mineralization).<sup>23</sup> GC analysis of the solution detected only a small amount of benzoic acid. The carbon balance for the identified products (benzaldehyde, benzoic acid, and  $CO_2$ ) is less than 50%, indicating that nonvolatile or thermally-degradable ring-opening products are involved as unidentified byproducts.

As shown in Table 1 (entry 9), benzaldehyde, when used as a starting material for photoreaction with  $TiO_2$  and  $O_2$  for 12 h, produces  $H_2O_2$  (8.6 mM), which is much lower than that obtained with benzyl alcohol (40 mM; entry 5). This clearly suggests that photocatalytic oxidation of benzaldehyde or its photoproducts is ineffective for  $H_2O_2$  formation;  $H_2O_2$  is efficiently produced during photocatalytic oxidation of benzyl alcohol to benzaldehyde.

Mechanism for Enhanced  $H_2O_2$  Production. Photocatalytic oxidation of alcohols with  $O_2$  on  $TiO_2$  occurs as Scheme 1. Photoexcited  $TiO_2$  (a) transfers  $e^-$  of lattice oxygen to adjacent  $Ti^{4+}$ , creating a charge-separated state (b). The  $e^-h^+$  pairs remove  $\alpha$ -hydrogen of alcohol<sup>24</sup> and produce an alcoholate species (c). Subsequent photoexcitation removes  $\beta$ -hydrogen of the

species<sup>24</sup> (d), producing a carbon radical (e). The  $e^-$  on the Ti<sup>3+</sup> site reduces  $O_2$  and produces a superoxo radical (f).<sup>12</sup> In the case with benzylic alcohol, the superoxo radical combines with adjacent carbon radical and produces O2-bridged complex (g). Heterolytic cleavage of the complex<sup>25</sup> produces the aldehyde with exchanged O atom and side-on coordinated peroxo species (h).<sup>26</sup> Protonation of the side-on peroxo species produces  $H_2O_2$ and completes the photocatalytic cycle. In contrast, with aliphatic alcohol, combination of carbon radical and superoxo radical does not occur efficiently (f), and the aldehyde is released without exchange of O atom (i).13 The superoxo radical left on the TiO<sub>2</sub> surface (i) is transformed to a hydroperoxo species (j) by further reduction with e (eq. 3). This is decomposed to OH<sup>-</sup> by further reduction with e<sup>-</sup> (eqs. 5 and 6). The above mechanisms indicate that photoexcitation of TiO2 with benzylic alcohol and O<sub>2</sub> specifically produces side-on peroxo species (h), via the heterolytic cleavage of O2-bridged complex (g). This peroxo species facilitates efficient and selective H<sub>2</sub>O<sub>2</sub> production.



**Figure 2.** Raman spectra of the  $TiO_2$  recovered after photoreaction in water with benzyl alcohol and (a)  ${}^{16}O_2$  or (b)  ${}^{18}O_2$ , and the  $TiO_2$ (c) recovered after photoreaction in water with ethanol and  ${}^{16}O_2$ . The reaction conditions are identical to those in Table 1.

The formation of side-on peroxo species (h) during reaction with benzylic alcohol is confirmed by Raman spectroscopy. The TiO<sub>2</sub> particles recovered after photoreaction (12 h) with alcohol and O<sub>2</sub> were used for analysis. Figure 2a shows the Raman spectrum of the TiO<sub>2</sub> particles recovered after photoreaction with benzyl alcohol and O<sub>2</sub> in water. Deconvolution of the spectrum exhibits three bands at 797, 830, and 894 cm<sup>-1</sup>. The 797 cm<sup>-1</sup> band is assigned to a first overtone of  $B_{1g}$  (397 cm<sup>-1</sup>) mode of anatase TiO<sub>2</sub>.<sup>27</sup> The 830 cm<sup>-1</sup> band is assigned to the C-O stretching vibration of the alcoholate species adsorbed on the TiO<sub>2</sub> surface (Scheme 1c).<sup>25</sup> The 894 cm<sup>-1</sup> band is assigned to the <sup>16</sup>O–<sup>16</sup>O stretching vibration of the side-on peroxo species

on the TiO<sub>2</sub> surface,<sup>25</sup> produced by heterolytic cleavage of O<sub>2</sub>bridged complex (Scheme  $1g \rightarrow h$ ). The heterolytic cleavage is confirmed by the spectrum of the TiO<sub>2</sub> recovered after photoreaction with benzyl alcohol and labeled molecular oxygen  $(^{18}O_2)$  in water. As shown in Figure 2b, new band is observed at  $870 \text{ cm}^{-1}$ , which is assigned to the  ${}^{16}\text{O}{-}^{18}\text{O}$  stretching vibration. The isotopic shift ( $\Delta = 24 \text{ cm}^{-1}$ ) is close to the shift (25 cm<sup>-1</sup>) calculated based on Hooke's law for a diatomic O-O stretching.<sup>28</sup> These data clearly suggest that, as shown in Scheme 1, photoreaction with benzylic alcohol produces O2-bridged complex (g) and its heterolytic cleavage creates side-on peroxo species (h).<sup>25</sup> It is noted that, as shown in Figure 2b, photoreaction of benzyl alcohol with  $^{18}\mathrm{O}_2$  shows a weak signal at 894  $\mathrm{cm}^{-1}$ assigned to the <sup>16</sup>O–<sup>16</sup>O side-on peroxide species. This is probably because the  ${}^{16}O-{}^{18}O$  side-on peroxide species formed on the photoactivated TiO<sub>2</sub> surface undergo O-exchange with the H<sub>2</sub><sup>16</sup>O molecules, as observed for related water systems.<sup>29</sup>

In contrast, as shown in Figure 2c, the TiO<sub>2</sub> particles recovered after photoreaction with ethanol and O<sub>2</sub> in water scarcely exhibits <sup>16</sup>O<sup>-16</sup>O band. This suggests that photoreaction with ethanol scarcely produces side-on peroxo species, and the result is consistent with the very low efficiency for H<sub>2</sub>O<sub>2</sub> production with ethanol (Table 1, entry 1). The above Raman spectroscopy data suggest that the formation of side-on peroxo species (Scheme 1h) is crucial for efficient H<sub>2</sub>O<sub>2</sub> formation. The formation of a large number of side-on peroxo species with benzylic alcohol is explained by the stabilization of carbon radical (Scheme 1f) due to the electron delocalization on the adjacent aromatic ring.<sup>30</sup> This facilitates efficient coupling between the carbon radical and superoxo species.

The stabilization of the carbon radical for benzylic alcohol depends strongly on the solvent polarity; highly polarized water is necessary for efficient formation of O2-bridged complex. Table 1 (entries 10-14) summarizes the results for photoreaction with benzyl alcohol in different organic solvents. All of these systems show H<sub>2</sub>O<sub>2</sub> selectivity lower than that obtained in water (entry 5). Figure 3 (•) shows the relationship between the empirical solvent polarity parameter,  $E_{\rm T}^{\rm N,31,32}$  of the solvents and the H<sub>2</sub>O<sub>2</sub> selectivity obtained by photoreaction in the respective solvents (Table 1, entries 5, 10-14). A linear relationship indicates that H<sub>2</sub>O<sub>2</sub> is selectively produced in more polar solvents. Figure 3 ( $\circ$ ) shows the relationship between the  $E_T^N$  of solvents and the intensity of <sup>16</sup>O-<sup>16</sup>O band for side-on peroxo species (I<sub>O-O</sub>) obtained by Raman analysis of TiO<sub>2</sub> after photoreaction with benzyl alcohol in the respective solvents (Figure S1, Supporting Information). The  $I_{O-O}$  increases with an increase in solvent polarity, and this tendency is consistent with the H<sub>2</sub>O<sub>2</sub> selectivity (•). These data suggest that polar solvents indeed enhance the formation of side-on peroxo species and produce H<sub>2</sub>O<sub>2</sub> more efficiently. The enhanced formation of side-on peroxo species is probably due to the stabilization of carbon radical in polar solvents<sup>30</sup> (Scheme 1f). This enhances the formation of O<sub>2</sub>-bridged complex (Scheme 1g) and creates larger number of side-on peroxo species (Scheme 1h), resulting in enhanced H<sub>2</sub>O<sub>2</sub> production in water.

Page 5 of 8

#### **ACS Catalysis**

60



**Figure 3.** (•) Relationship between  $E_T^N$  of solvents and the  $H_2O_2$  selectivity obtained by photoreaction with benzyl alcohol and  $O_2$  (12 h) in the respective solvents (Table 1). (•) Relationship between  $E_T^N$  of solvents and the intensity ( $I_{O-O}$ ) of side-on coordinated peroxo species (894 cm<sup>-1</sup>) on the TiO<sub>2</sub> recovered after photoreaction in the respective solvents (Figure S1, Supporting Information).  $I_{O-O} = [\{\text{intensity of 894 cm}^{-1} \text{ band in respective solvents}\} \times \{\text{amount of benzyl alcohol consumed in water}\}] / [\{\text{intensity of 894 cm}^{-1} \text{ band in respective solvents}\}].$ 



**Figure 4.** ESR spectra (298 K) of DMPO spin adduct in the solutions obtained by photoirradiation of TiO<sub>2</sub> with benzyl alcohol and O<sub>2</sub> in (a) CH<sub>3</sub>CN, (b) CH<sub>3</sub>CN/water (7/3 v/v) mixture, and (c) water, and (d) the solution obtained by photoirradiation of TiO<sub>2</sub> with ethanol and O<sub>2</sub> in water. Reaction conditions: solvent (5 mL), TiO<sub>2</sub> (50 mg), alcohol (1.75 mmol), DMPO (0.1 mmol), O<sub>2</sub> (1 atm), photoirradiation time (15 min).

The photoreaction mechanism summarized in Scheme 1 is supported by ESR analysis. Figure 4 shows the ESR spectra of the solution recovered after photoirradiation of TiO<sub>2</sub> with benzyl alcohol and O<sub>2</sub> in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO), a spin trapping reagent. With less polar CH<sub>3</sub>CN as a solvent (Figure 4a), distinctive signals assigned to the DMPO-O<sub>2</sub><sup>•</sup> spin adduct<sup>33</sup> were observed ( $\alpha_N = 12.7 \text{ G}; \alpha_H^{\beta} = 8.5 \text{ G}; g = 2.0065$ ). This suggests that, as shown in Scheme 1i, the superoxo radical is produced during photoreaction with benzylic alcohol in less polar solvents and is trapped by the reaction with DMPO.

$$Ti^{4+} - O - O^{\bullet} + DMPO \rightarrow Ti^{4+} + DMPO - O_2^{\bullet-}$$
(7)

The intensity of the spin adduct signal decreases with an increase in the solvent polarity, and almost no signal is observed in water (Figure 4c). In contrast, as shown in Figure 3 ( $\circ$ ), the formation of side-on peroxo species is enhanced with an increase in the solvent polarity. These data suggest that, during photoreaction with benzyl alcohol in less polar solvents (Scheme 1), the carbon radical (f) is rapidly removed and leaves superoxo radical (i), whereas the photoreaction in polar water produces O<sub>2</sub>-bridged complex (g) and results in enhanced formation of side-on peroxo species (h).

Figure 4d shows the ESR spectrum of water obtained after photoreaction with ethanol and O2. The signals for DMPO- $O_2^{\bullet-}$  spin adduct were observed ( $\alpha_N = 15.1 \text{ G}; \alpha_H^{\beta} = 9.5 \text{ G}; g =$ 2.0061), with signals assigned to DMPO- $^{\bullet}$ OH spin adduct ( $\alpha_{N}$ = 14.2 G;  $\alpha_{\rm H}^{\ \beta}$  = 14.0 G; g = 2.011),<sup>34</sup> which is produced by oxidation of water on the photoactivated TiO\_2 (OH^- +  $\rm h^+ \rightarrow$  $^{\circ}$ OH).<sup>35</sup> The formation of the DMPO-O<sub>2</sub> $^{\circ-}$  spin adduct signal suggests that, during photoreaction with aliphatic alcohol (Scheme 1), the carbon radical (f) is rapidly removed and leaves superoxo radical (i), resulting in very low efficiency for H<sub>2</sub>O<sub>2</sub> formation. These data fully support the proposed mechanism (Scheme 1). Photoexcitation of TiO<sub>2</sub> with alcohol and O<sub>2</sub> produces a set of carbon radical and superoxo radical (f). In water with benzylic alcohol, the carbon radical is stabilized and transformed to O2-bridged complex. This produces a large number of side-on peroxo species and efficiently produces H2O2. In contrast, with aliphatic alcohol or with benzylic alcohol in less polar solvents, the carbon radical is unstable and is removed rapidly. This leaves superoxo radical to be decomposed by subsequent reaction, resulting in very low efficiency for H<sub>2</sub>O<sub>2</sub> formation. These findings suggest that benzylic alcohol and water are necessary for efficient and selective  $H_2O_2$  formation.

#### CONCLUSION

We found that photoexcitation of anatase  $\text{TiO}_2$  in water with benzylic alcohol and  $\text{O}_2$  efficiently promotes  $\text{H}_2\text{O}_2$  formation. This system successfully produces very high concentration of  $\text{H}_2\text{O}_2$  (ca. 40 mM), which is much higher than those of early reported photocatalytic systems with aliphatic alcohols. The enhanced  $\text{H}_2\text{O}_2$  formation is due to the efficient formation of side-on peroxo species produced via the reaction of benzylic alcohols and  $\text{O}_2$  in water. The present  $\text{H}_2\text{O}_2$  selectivity is ca. 33%, and further improvement of the selectivity is necessary. Nevertheless, the concept presented here based on the selective creation of side-on coordinated peroxo species on the  $\text{TiO}_2$ surface may contribute to the design of more efficient and selective photocatalytic systems for  $H_2O_2$  production and may open a new strategy towards clean and safe  $H_2O_2$  synthesis without  $H_2$  gas.

## EXPERIMENTAL SECTION

Photoreaction. TiO<sub>2</sub> (50 mg) was suspended in a solution (5 mL) containing each respective alcohol (1.75 mmol) within a glass tube ( $\varphi$ 12 mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and O2 was bubbled through the solution for 5 min. The tube was photoirradiated at  $\lambda$  >280 nm with magnetic stirring using a 450 W high pressure Hg lamp (USHIO Inc.).<sup>17</sup> Visible light ( $\lambda$  >420 nm) irradiation was carried out with an aqueous NaNO2 (20 wt%) solution as a filter.<sup>36</sup> The temperature of solution was kept at 298 ± 0.5 K with a digitally-controlled water bath.<sup>21</sup> The gas-phase product was analyzed by GC-TCD (Shimadzu; GC-14B). The catalyst was recovered by centrifugation, and the liquid-phase product was analyzed by GC-FID (Shimadzu; GC2010A). The substrate and product concentrations were calibrated with authentic samples. H<sub>2</sub>O<sub>2</sub> concentration was determined by the redox titration with KMnO<sub>4</sub>.<sup>23</sup>

**Quantum yield determination.** Photoreaction was carried out using a water (2 mL) containing alcohol (0.7 mmol) and TiO<sub>2</sub> (20 mg) within a glass tube ( $\varphi$  12 mm; capacity, 20 mL). After ultrasonication and O<sub>2</sub> bubbling, the tube was photoirradiated with stirring using a Xe lamp (USHIO Inc.)<sup>23</sup> for 3 h, where the incident light was monochromated by a 334 nm band-pass glass filter (Asahi Techno Glass Co.; LX334). The full-width at half-maximum (fwhm) of the light was 9 nm. The photon number entered into the reaction vessel was determined with a spectroradiometer USR40 (USHIO Inc.)<sup>37</sup>

**Raman spectroscopy.** Raman spectra were measured on a confocal Raman microscope (LabRAM HR-800, HORIBA). YAG laser (532 nm line) was used as the excitation source, where the laser power was 100 mW and the total data accumulation time was 30 s. The samples were prepared as follows: After photoreaction, TiO<sub>2</sub> particles were recovered by centrifugation and dried at room temperature in vacuo. They were mounted on a microscope slide and subjected for analysis. The peak intensities were normalized to the peak at 797 cm<sup>-1</sup> for a first overtone of  $B_{1v}$  mode for anatase TiO<sub>2</sub>.

**ESR measurement.** ESR spectra were recorded at the X-band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 10.5 mW, where microwave power saturation of the signals does not occur.<sup>22</sup> The magnetic field was calibrated using a 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as standard. The measurement was carried out as follows: TiO<sub>2</sub> (50 mg) was suspended in a solution (5 mL) containing each respective alcohol (1.75 mmol) and DMPO (0.1 mmol) within a glass tube ( $\varphi$ 12 mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. After ultrasonication (5 min) and O<sub>2</sub> bubbling (5 min), the solution was photoirradiated ( $\lambda > 280$  nm) for 15 min with magnetic stirring. The catalyst was recovered by centrifugation, and the resulting solution was subjected to analysis.

#### ASSOCIATED CONTENT

Raman spectra of TiO<sub>2</sub> recovered after photoreaction with benzyl alcohol in different solvents (Figure S1), results of photocatalytic  $H_2O_2$  production on various TiO<sub>2</sub> (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

## **Corresponding Author**

shiraish@cheng.es.osaka-u.ac.jp

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENT

This work was supported by the Grant-in-Aid for Scientific Research (No. 23360349) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

## REFERENCES

(1) Campos-Martin, J. M.; Blanco-Brieva, G.; Fierro, J. L. G. Angew. Chem., Int. Ed. 2006, 45, 6962–6984.

(2) Lunsford, J. H. J. Catal. 2003, 216, 455-460.

(3) Blanco-Brieva, G.; Cano-Serrano, E.; Campos-Martin, J. M.; Fierro, J. L. G. Chem. Commun. 2004, 1184–1185.

(4) Melada, S.; Rioda, R.; Menegazzo, F.; Pinna, F.; Strukul, G. J. Catal. 2006, 239, 422-430.

(5) Choudhary, V. R.; Gaikwad, A. G.; Sansare, S. D. Angew. Chem., Int. Ed. 2001, 40, 1776-1779.

(6) Landon, P.; Collier, P. J.; Papworth, A. J.; Kiely, C. J.; Hutchings, G. J. Chem. Commun. 2002, 2058–2059.

(7) Edwards, J. K.; Solsona, B.; Ntainjua, E.; Carley, A. F.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. Science 2009, 323, 1037-1041.

(8) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. Environ. Sci. Technol. 1988, 22, 798-806.

(9) Cai, R.; Kubota, Y.; Fujishima, A. J. Catal. 2003, 219, 214-218.

(10) Goto, H.; Hanada, Y.; Ohno, T.; Matsumura, M. J. Catal. 2004, 225, 223-229.

(11) Hirakawa, T.; Nosaka, Y. J. Phys. Chem. C 2008, 112, 15818-15823.

(12) Nakamura, R.; Imanishi, A.; Murakoshi, K.; Nakato, Y. J. Am. Chem. Soc. 2003, 125, 7443-7450.

(13) Hirakawa, T.; Koga, C.; Negishi, N.; Takeuchi, K.; Matsuzawa, S. Appl. Catal. B **2009**, 87, 46–55.

(14) Hirakawa, T.; Daimon, T.; Kitazawa, M.; Ohguri, N.; Koga, C.; Negishi, N.; Matsuzawa, S.; Nosaka, Y. J. Photochem. Photobiol. A 2007, 190, 58-68.

(15) Maurino, V.; Minero, C.; Mariella, G.; Pelizzetti, E. Chem. Commun. 2005, 2627-2629.

(16) Teranishi, M.; Naya, S.; Tada, H. J. Am. Chem. Soc. 2010, 132, 7850-7851.

(17) Tsukamoto, D.; Shiro, A.; Shiraishi, Y.; Sugano, Y.; Ichikawa,

S.; Tanaka, S.; Hirai, T. ACS Catal. 2012, 2, 599-603.

(18) Li, X.; Chen, C.; Zhao, J. *Langmuir* 2001, *17*, 4118-4122.

(19) Higashimoto, S.; Kitao, N.; Yoshida, N.; Sakura, T.; Azuma, M.; Ohue, H.; Sakata, Y. J. Catal. **2009**, *266*, 279–285.

(20) Tanaka, K.; Capule, M. F. V.; Hisanaga, T. Chem. Phys. Lett. 1991, 187, 73-76.

(21) Tsukamoto, D.; Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. J. Am. Chem. Soc. **2012**, *134*, 6309–6315.

(22) Sugano, Y.; Shiraishi, Y.; Tsukamoto, D.; Ichikawa, S.; Tanaka, S.; Hirai, T. Angew. Chem. Int. Ed. **2013**, *52*, 5295–5299.

1

## **ACS Catalysis**

2
3
4
-
5
6
7
8
9
10
10
11
12
13
14
15
16
10
17
18
19
20
21
20
22
23
24
25
26
20
21
28
29
30
31
32
22
33
34
35
36
37
20
30
39
40
41
42
43
11
44 45
45
46
47
48
40
-3 50
50
51
52
53
54
55
00
56
57
58
50

(23) Tsukamoto, D.; Ikeda, M.; Shiraishi, Y.; Hara, T.; Ichikuni, N.;
Tanaka, S.; Hirai, T. Chem. Eur. J., 2011, 17, 9816-9824.
(24) Shishido, T.; Miyatake, T.; Teramura, K.; Hitomi, Y.; Yamashita,
H.; Tanaka, T. J. Phys. Chem. C 2009, 113, 18713–18718.
(25) Zhang, M.; Wang, Q.; Chen, C.; Zang, L.; Ma, W.; Zhao, J.
Angew. Chem. Int. Ed. 2009, 48, 6081–6084.
(26) Jeske, P.; Haselhorst, G.; Weyhermüeller, T.; Wieghardt, K.;
Nuber, B. Inorg. Chem. 1994, 33, 2462-2471.
(27) Tompsett, G. A.; Bowmaker, G. A.; Cooney, R. P.; Metson, J.
B.; Rodgers, K. A.; Seakins, J. M. J. Raman Spectrosc. 1995, 26, 57-62.

- (28) Tsilomelekis, G.; Boghosian, S. J. Phy. Chem. C 2011, 115, 2146-2154.
- (29) Risley, J. M.; Van Etten, R. L. J. Am. Chem. Soc. 1981, 103, 4389-4392.
- (30) Ito, O.; Matsuda, M. J. Am. Chem. Soc. 1982, 104, 568–572.
  (31) Reichardt, C. Chem. Rev. 1994, 94, 2319–2358.
- (32) Johnson, B. P.; Khaledi, M. G.; Dorsey, J. G. Anal. Chem. 1986,
- (32) Jonnson, B. P.; Knaledi, M. G.; Dorsey, J. G. Anal. Chem. 1986 58, 2354–2365.
- (33) Wang, W.; Ng, T. W.; Ho, W. K.; Huang, J.; Liang, S.; An, T.; Li, G.; Yu, J. C.; Wong, P. K. Appl. Catal. B **2013**, *129*, 482-490.
- (34) Lin, F.; Zhang, Y.; Wang, L.; Zhang, Y.; Wang, D.; Yang, M.;
  Yang, J.; Zhang, B.; Jiang, Z.; Li, C. Appl. Catal. B 2012, 127, 363–370.
  (35) Hirakawa, T.; Nosaka, Y.; Langmuir 2002, 18, 3247–3254.
- (36) Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Hirai, T. Catal. Sci. Technol. 2012, 2, 400-405.
- (37) Koizumi, H.; Shiraishi, Y.; Tojo, S.; Fujitsuka, M; Majima, T.; Hirai, T. J. Am. Chem. Soc. **2006**, 128, 8751-8753.

# SYNOPSIS TOC

Selective Hydrogen Peroxide Formation by Titanium Dioxide Photocatalysis with Benzylic Alcohols and Molecular Oxygen in Water

Yasuhiro Shiraishi,\* Shunsuke Kanazawa, Daijiro Tsukamoto, Akimitsu Shiro, Yoshitsune Sugano, and Takayuki Hirai

