Highly Active Rutile TiO$_2$ for Photocatalysis under Violet Light Irradiation at 405 nm

Fumiaki Amano $^{1,*}$, Akira Yamamoto $^{2}$ and Jun Kumagai $^{3}$

$^1$ Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan
$^2$ Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-Nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan
$^3$ Institute of Materials and Systems for Sustainability, Division of Materials Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
* Correspondence: f.amano@tmu.ac.jp

Abstract: Anatase TiO$_2$ is a widely investigated photocatalyst; however, it can only work under ultraviolet (UV) light with wavelengths less than 390 nm (band gap 3.2 eV). Rutile TiO$_2$ can absorb visible light at wavelengths less than 410 nm (band gap 3.0 eV); however, its photocatalytic activity is not high. Herein, we activated rutile TiO$_2$, which was prepared from Evonik TiO$_2$ P 25 through calcination at 800 $^\circ$C using hydrogen reduction treatment at 700 $^\circ$C. The photocatalytic activity of the hydrogen-treated TiO$_2$ was as high as P 25 under UV irradiation at 380 nm, which was significantly higher than P 25 under violet light irradiation at 405 nm for the oxidative decomposition of acetic acid in water. Electron spin resonance studies indicate that charge separation is enhanced in reduced TiO$_2$, and their oxygen reduction pathways differ between anatase and rutile. The formation of H$_2$O$_2$ was observed on rutile TiO$_2$; however, it was consumed during photocatalysis to accelerate acetic acid decomposition.

Keywords: blue titania; electron paramagnetic resonance; ESR; hydrogen peroxide; mineralization; oxygen reduction reaction; titanium dioxide; Ti$^{3+}$ species; visible light

1. Introduction

Titania (TiO$_2$) is one of the most investigated photocatalytic materials for the environmental purification of air and water under ultraviolet (UV) light irradiation [1–4]. There are several studies on the photocatalytic activity of anatase TiO$_2$ for the oxidative decomposition of organic pollutants in air and water. In contrast, rutile TiO$_2$ has not been extensively studied due to the lower photocatalytic activity in the presence of O$_2$ as an oxidizing species [5–7]. However, rutile can be effectively used in photocatalytic applications because it can absorb violet light in the visible region owing to the band gap energy ($E_g$ = 3.2 eV, onset wavelength $\lambda_{onset}$ = 413 nm) being narrower than that of anatase ($E_g$ = 3.0 eV, $\lambda_{onset}$ = 388 nm) [3,8].

High photocatalytic activities are frequently reported for anatase TiO$_2$ with a high specific surface area [3,9]. Anatase TiO$_2$ irreversibly transforms into rutile, which is in a thermodynamically stable phase, through high-temperature calcination (Figure 1a). However, this heat treatment at high temperatures decreased the specific surface area due to the increase in the particle size and decreased photocatalytic activity. The surface OH groups also decreased under thermal treatment. The decrease in surface OH group density has been correlated with the lower photocatalytic activity of TiO$_2$ [5,10,11].

The low photocatalytic activity of rutile TiO$_2$ is also explained by the energy level of the conduction band minimum (CBM) of rutile, which is less than that of anatase (Figure 1b) [5]. Electrochemical studies indicate that the flat band potential, which is located just under the CBM for an n-type semiconductor, of rutile TiO$_2$(001) is more positive than that of
anatase TiO₂(101) by 0.2 V [8]. This may affect the electron transfer to oxygen, which is the rate-determining process in photocatalysis [12–14]. The position of the CBM of rutile implies that a one-electron reduction in O₂ with conduction band electrons (e⁻_{cb}) to form superoxide radical anions (O₂•⁻) may be difficult to achieve in rutile (Figure 1b).

Figure 1. (a) Effect of calcination temperature on the properties of TiO₂. (b) Schematic energy diagram of anatase and rutile TiO₂ and the standard electrode potentials for the oxygen reduction reaction. The conduction band (CB) minimum positions were assumed from the reported flat band potentials, and the valence band (VB) maximum positions were derived from their band gap energies.

In addition, several reports have concluded that the recombination of photogenerated carriers is likely to occur in rutile TiO₂ [15–17]. The electron mobility of rutile is less than that of anatase [18,19]. The difference in the depth of electron traps has also been elucidated by time-resolved visible and infrared absorption spectroscopies [15].

Nevertheless, it has been revealed that H₂ reduction treatment improves the photocatalytic and photoelectrochemical activities of rutile TiO₂ [20–26]. However, the application of H₂-treated rutile TiO₂ has been limited for photocatalytic oxidative decomposition of organic compounds since it is believed that rutile is not active for photocatalysis with oxygen reduction. In this study, we investigated the photocatalysis of H₂-treated rutile TiO₂ for the mineralization of acetic acid to carbon dioxide (CO₂). Acetic acid is one of the most studied model compounds for the photocatalytic mineralization of organic pollutants and intermediates during the oxidative decomposition of acetaldehyde. Herein, we firstly found that the H₂-treated rutile TiO₂ exhibited high photocatalytic activity for the oxidative decomposition reaction even under violet light irradiation (405 nm). We explored the mechanism for enhanced photocatalytic activity using electron spin resonance (ESR) spectroscopy and quantification of hydrogen peroxide (H₂O₂) during the photocatalytic reactions.

2. Results
2.1. Preparation and Characterization

We used Evonik/Degussa Aeroxide® P 25, which is a commercial TiO₂ with high photocatalytic activity [27], with varying compositions of anatase (~85%) and rutile (~15%) [28]. P 25 powder was calcined in air at 800 °C for 2 h. Thus-obtained P800 was further treated with H₂ flow at 700 °C for 2 h. The H₂-treated TiO₂ is denoted as P800-H700.

Figure 2 shows the scanning electron microscope (SEM) images of the TiO₂ samples. The particle size increased from ~30 to ~100 nm after calcination. In contrast, the hydrogen treatment did not change the particle size of P800. These phenomena were supported by the BET-specific surface areas (SSA_{BET}), which were 55, 9.6, and 9.8 m² g⁻¹ for P 25, P800, and P800-H700, respectively.
which was added to 30 wt% as an internal standard. P 25 was composed of anatase (87%) and rutile (13%) [24,29]. Calcination at 800 °C converted anatase to pure rutile (100%). P800-H700 also consisted of a single phase of rutile TiO₂.

Figure 3 shows powder X-ray diffraction (XRD) patterns of TiO₂ with nickel oxide, which was added to 30 wt% as an internal standard. P 25 was composed of anatase (87%) and rutile (13%) [24,29]. Calcination at 800 °C converted anatase to pure rutile (100%). P800-H700 also consisted of a single phase of rutile TiO₂.

2.2. Optical Properties of TiO₂ Particles

Figure 4a shows the diffuse reflectance UV-visible spectra using barium sulfate as a reference. The optical absorption onset (λ onset) of P 25 was exhibited at ~410 nm, which is consistent with 3.02 eV of rutile TiO₂. However, the absorption edge of P 25 was not steep because rutile was not the major phase in P 25. P800 and P800-H700 exhibited steeper absorption edges than P 25. The λ onset of P800 and P800-H700 was ~415 nm (2.99 eV), which is consistent with the Eₗ of rutile TiO₂ [8,30,31].

As shown in Figure 4b, P800 was white, whereas P800-H700 was pale blue. This blue color is related to visible light absorption. The 1—reflectance values at wavelengths longer than 420 nm were not zero for all samples. However, the values of P 25 and P800 originate from scattering. In contrast, the extinction of P800-H700 is attributed to electron transitions from the shallow traps in Ti³⁺-enriched TiO₂ [32–34]. The blue TiO₂ implies the formation of partially reduced TiO₂ with Ti³⁺ species.

Figure 2. FE-SEM images of TiO₂ particles (P 25, P800, and P800-H700).

Figure 3. XRD patterns of TiO₂ powders mixed with NiO as an internal standard: (●) Rutile TiO₂, (▲) anatase TiO₂, and (■) NiO.
2.3. Photocatalytic Activity Test

Figure 5 shows the time course of photocatalytic CO$_2$ evolution through the decomposition of acetic acid in water. CO$_2$ evolution was effectively induced by the highly active P 25 and P800-H700 under UV illumination at 380 nm. In contrast, CO$_2$ evolution over P800 was sluggish because of the phase transformation to rutile. The decreased activity may be explained by the decrease in the specific surface area. However, P800-H700 with low SSA$_{BET}$ (9.8 m$^2$ g$^{-1}$) also exhibited high activity, which is comparable to that of highly active P 25 (SSA$_{BET}$ = 55 m$^2$ g$^{-1}$). This implies that the intrinsic activity per unit surface area was significantly high for H$_2$-treated rutile TiO$_2$.

![Graph showing photocatalytic CO$_2$ evolution](image)

**Figure 5.** Photocatalytic CO$_2$ evolution through oxidative decomposition of acetic acid under (a) 380-nm UV irradiation (9 mW cm$^{-2}$) and (b) 405-nm violet light irradiation (18 mW cm$^{-2}$). Photocatalyst: 50 mg, liquid phase: 1 vol% CH$_3$COOH aq. (9.0 mL), gas phase: Oxygen (15 mL), and temperature 25°C.

Figure 5b shows the results of the photocatalytic reaction under violet light at 405 nm. In this visible light region, the photocatalytic activity of P 25 was very low because the...
main component of anatase could not absorb violet light. The CO₂ evolution of P 25 was as low as P800 under 405-nm irradiation. In contrast, P800-H700 exhibited significantly higher photocatalytic activity than anatase-rich P 25 and conventional rutile TiO₂. Rutile can absorb violet light; however, its photocatalytic activity is generally less than that of anatase. However, H₂-treated rutile exhibited high photocatalytic activity even in the violet light region. The apparent quantum efficiencies of CO₂ evolution were 8.4% at 380 nm and 4.9% at 405 nm when four electrons were required for one molecule of CO₂ formation (CH₃COOH + 2H₂O → 2CO₂ + 8H⁺ + 8e⁻).

2.4. ESR Study

To determine the reason for the enhanced activity, we measured the ESR spectra of H₂-reduced rutile (Figure 6). The signal assigned to the Ti³⁺ species at g = 2.0–1.8 was not observed for P800. In contrast, P800-H700 exhibited a broad signal of Ti³⁺ at g = 2.0–1.8. The signal at g⊥ = 1.97 is assigned to Ti³⁺ in rutile TiO₂ [35,36]. The signal broadening in H₂-reduced TiO₂ suggests a magnetic dipole–dipole interaction due to the high density of Ti³⁺ species [34].

![Figure 6](image)

**Figure 6.** (a) ESR spectra of P800 and P800-H700 with helium (18 Torr) at −253 °C. (b) Difference spectra between before and after UV irradiation at 365 nm.

When the sample was exposed to UV light, the signal changed slightly. The different spectra before and after UV irradiation indicate an increase in Ti³⁺ and the formation of photogenerated holes trapped on the lattice oxygen atom (O₁•−) with g values in the range of 2.02–2.00. The increment in the signal intensities was higher for P800-H700 than for P800, suggesting more efficient charge separation in H₂-reduced rutile TiO₂ under UV irradiation. The longer lifetime of the trapped electrons indicates the high activity of P800-H700.

We further investigated the oxygen reduction reaction over anatase and rutile TiO₂ using ESR spectroscopy (Figure 7). After evacuation, P 25 exhibits a signal at g = 1.98, which is assigned to the Ti³⁺ in anatase TiO₂ [35,36]. A signal intensity less than that of P800-H700 indicates the low density of Ti³⁺ in P 25. In the presence of molecular oxygen (1.0 Torr), there are several signals of paramagnetic O₂ exhibited in the gas phase (Figure S1 in the Supplementary Materials) [37]. Under UV irradiation, P 25 exhibited signals at g = 2.04–1.98. The line shape was not resolved and was superimposed on several
radicals. The superoxide anion (O$_2$$^ {•-}$) on anatase can be identified as $g_1 = 2.020$–2.029, $g_2 = 2.009$, and $g_3 = 2.003$ [38–43]. When photogenerated e$_{cb}$$^ {•-}$ is used for O$_2$ reduction, the valence band hole is trapped on the surface (O$_L$$^ {•-}$). The $g$-values of O$_L$$^ {•-}$ in anatase were $g_1 = 2.016$, $g_2 = 2.012$, and $g_3 = 2.002$ [35,38,39]. Therefore, we assigned the unresolved signals to O$_2$$^ {•-}$ and O$_L$$^ {•-}$ to anatase. However, the O$_2$$^ {•-}$ signal was not formed for P800-H700, even under UV irradiation. The weak and broad signal at $g = 2.015$ can be assigned to O$_L$$^ {•-}$ on rutile. The absence of the O$_2$$^ {•-}$ signal suggests that a one-electron reduction pathway (O$_2$ + e$_{cb}$$^ {•-}$ → O$_2$$^ {•-}$) does not occur in Ti$^{3+}$-rich rutile (P800-H700). A similar result was reported for the Bi$_2$WO$_6$ photocatalyst [44].

2.5. Effect of H$_2$O$_2$ Addition on the Photocatalytic Activity

The fact that one-electron oxygen reduction was not involved in the photocatalysis of rutile TiO$_2$ motivated us to confirm the presence of a two-electron pathway (O$_2$ + 2H$^ {+}$ + 2e$_{cb}$$^ {•-}$ → H$_2$O$_2$). Table 1 summarizes the formation of H$_2$O$_2$ during the photocatalytic reaction of acetic acid decomposition. H$_2$O$_2$ was analyzed by the colorimetric method using the oxidation of iodide to triiodide ions (Equations (1) and (2)) [45–47].

\[
\begin{align*}
H_2O_2 + 2H^ {+} + 2I^- & \rightarrow 2H_2O + I_2 \\
I_2 + I^- & \rightarrow I_3^-
\end{align*}
\]

Table 1. Photocatalytic reaction in 1 vol% CH$_3$COOH aqueous solution after violet light irradiation for 20 min.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Formed H$_2$O$_2$/µmol</th>
<th>Evolved CO$_2$/µmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 25</td>
<td>0.17</td>
<td>1.19</td>
</tr>
<tr>
<td>P800</td>
<td>0.03</td>
<td>0.88</td>
</tr>
<tr>
<td>P800-H700</td>
<td>0.09</td>
<td>3.36</td>
</tr>
<tr>
<td>blank</td>
<td>–</td>
<td>0.00</td>
</tr>
</tbody>
</table>

![Figure 7. ESR spectra at −150 °C of (a) P 25 and (b) P800-H700. The sample was measured after (i) evacuation at 25 °C for 1 h, (ii) introduction of 1.0 Torr of oxygen, and (iii) UV irradiation with oxygen. The difference spectra between before and after photoirradiation are also shown.](image-url)
We confirmed that H$_2$O$_2$ was formed in the photocatalytic reaction over 20 min; however, the formed amount was significantly low for P800-H700 (Table 1). Because H$_2$O$_2$ is easily decomposed, we investigated the degradation behavior of H$_2$O$_2$ under photocatalytic conditions. Table 2 summarizes the effect of the presence of 9 µmol of H$_2$O$_2$ in the feed. Without TiO$_2$ photocatalysts, H$_2$O$_2$ did not decompose even under light irradiation. In contrast, the added H$_2$O$_2$ did not remain after 20 min of photocatalysis over Ti$^{3+}$-rich rutile TiO$_2$. This fast degradation can explain the low amount of H$_2$O$_2$ formed during the photocatalytic reaction. Notably, CO$_2$ evolution was significantly enhanced by the H$_2$O$_2$ addition for P800-H700. This suggests that H$_2$O$_2$ promotes the decomposition of acetic acid over the Ti$^{3+}$-rich rutile TiO$_2$.

**Table 2.** Photocatalytic reaction in 1 vol% CH$_3$COOH aqueous solution with 9 µmol H$_2$O$_2$ after violet light irradiation for 20 min.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Residual H$_2$O$_2$/µmol</th>
<th>Evolved CO$_2$/µmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 25</td>
<td>2.93</td>
<td>0.89</td>
</tr>
<tr>
<td>P800</td>
<td>1.48</td>
<td>2.39</td>
</tr>
<tr>
<td>P800-H700</td>
<td>0.03</td>
<td>8.60</td>
</tr>
<tr>
<td>blank</td>
<td>9.39</td>
<td>0.00</td>
</tr>
</tbody>
</table>

3. Discussion

The flat band potential of rutile TiO$_2$ is reported to be +0.05 or +0.13 V vs. the standard hydrogen electrode (SHE) [30,31]. The flat band potential of anatase is more negative than that of rutile TiO$_2$ by 0.20–0.26 eV [8,48]. Thus, the CBM of anatase and rutile is roughly assumed to be located at approximately −0.2 and 0 V vs. SHE (Figure 1b). To reduce oxygen, the CBM should be more negative than the standard electrode potentials of the oxygen reduction reactions, as expressed in Equations (3)–(5) [49].

\[
\begin{align*}
\text{O}_2 + e^- &= \text{O}_2^{•−}, \ E^o = -0.33 \text{ V vs. SHE} \quad (3) \\
\text{O}_2 + \text{H}^+ + e^- &= \text{HO}_2^{•}, \ E^o = -0.046 \text{ V vs. SHE} \quad (4) \\
\text{O}_2 + 2\text{H}^+ + 2e^- &= \text{H}_2\text{O}_2, \ E^c = +0.695 \text{ V vs. SHE} \quad (5)
\end{align*}
\]

As shown in Figure 1, the CBM of anatase is close to or more negative than the thermodynamic theoretical potential for one-electron reduction to form oxygen radicals (O$_2^{•−}$ and HO$_2^{•}$). In contrast, the CBM of rutile TiO$_2$ cannot promote one-electron reduction, as demonstrated by ESR. Nevertheless, two-electron reduction of oxygen is thermodynamically possible for rutile. In addition, the formation of H$_2$O$_2$ during the photocatalytic reaction was confirmed (Table 1). H$_2$O$_2$ formation has also been reported in Pt-WO$_3$ and Bi$_2$WO$_6$ photocatalysts with deep CBM [46,47,50].

The low amount of H$_2$O$_2$ during photocatalysis can be explained by the rapid degradation by the e$_{cb}^-$ in the rutile photocatalyst, as expressed in Equation (6) [46,49].

\[
\text{H}_2\text{O}_2 + e^- = \text{•OH} + \text{OH}^−, \ E^o = +1.14 \text{ V vs. SHE} \quad (6)
\]

The in situ-generated H$_2$O$_2$ can act as an electron scavenger to retard the recombination of photogenerated carriers [50]. The reaction of e$_{cb}^-$ with H$_2$O$_2$ is easier than with O$_2$. Moreover, the hydroxyl radical (•OH) formed is a very strong oxidant (E$^o$ = +2.38 V vs. SHE), thus promoting acetic acid degradation [5,10,51]. This hypothesis agrees with the enhanced CO$_2$ formation by adding H$_2$O$_2$ (Table 2).

Figure 8 illustrates the proposed reaction scheme for a highly active rutile TiO$_2$ photocatalyst for the oxidative decomposition of acetic acid. It can be observed that charge separation is enhanced in the Ti$^{3+}$-rich rutile under UV and violet light irradiation (λ < ~415 nm). The photogenerated hole can oxidize acetic acid to the CH$_3$COO$^*$ radical, which will be •CH$_3$ radical vis decarboxylation [52]. The two-electron reduction of oxygen by e$_{cb}^-$ is the
Moreover, the hydroxyl radical (•OH) formed is a very strong oxidant ($E^\circ = +2.38 \text{ V vs. NHE}$). The ESR sample tube was irradiated using an ultra-high-pressure mercury lamp with a 365 nm band path filter. A JEOL JES-RE1X (Akishima, Japan) was used for the oxygen reduction reaction at $-150 \degree C$. UV irradiation was performed using a xenon lamp through a 365 nm band path filter. The samples were pre-evacuated at room temperature for 60 min on a vacuum line before the ESR measurements, and oxygen gas (1.0 Torr) was added to the ESR sample tube at 25 $\degree C$.

### 4. Materials and Methods

Evonik/Degussa Aerioxide TiO$_2$ P 25 was obtained from Nippon Aerosil Co. (Yokkaichi, Japan). Calcination in air was performed in an alumina crucible in an electric furnace at 800 $\degree C$ for 2 h. The treatment under H$_2$ flow (50 mL min$^{-1}$) was performed in a quartz boat using a quartz tube-type reactor at 700 $\degree C$ for 2 h. The temperature was naturally cooled to 300 $\degree C$ under H$_2$ flow and to room temperature under N$_2$ flow (100 mL min$^{-1}$).

SEM images were recorded using a Hitachi S-5200 field emission scanning electron microscope (Tokyo, Japan). The BET-specific surface areas were determined at $-196 \degree C$ using a MicrotracBEL Belsorp-mini instrument (Osaka, Japan). The XRD patterns were recorded using a Rigaku RINT-2000 diffractometer (Akishima, Japan). UV-visible spectra were obtained using an ALS SEC2000-UV/vis spectrometer (Tokyo, Japan) with a Hamamatsu Photonics L10290 fiber light source (Hamamatsu, Japan).

The photocatalytic activity was examined by measuring CO$_2$ evolution from an aqueous solution of 1 vol% acetic acid. The reactor was a glass test tube with an outer diameter of 18 mm and the volume of the liquid was 9.0 mL. A suspension of 50 mg TiO$_2$ particles was sonicated for 1 min and bubbled with oxygen for 5 min. After stirring for 30 min in the dark, photoirradiation was performed using a LED at 25 $\degree C$. The evolved CO$_2$ was detected using a TCD-GC with a Porpak-Q column and helium carrier. The concentration of H$_2$O$_2$ was quantified from the UV-visible spectra of I$_3^-$ formed from H$_2$O$_2$ (2 mL), 0.2 M KI (1 mL), and 0.2 M H$_2$SO$_4$ (1 mL) at 25 $\degree C$. The absorbance of I$_3^-$ was measured at 351 nm wavelength.

The ESR spectra were recorded at $-253 \degree C$ using liquid helium on a JEOL JES-RE1X (Akishima, Japan). The ESR sample tube was irradiated using an ultra-high-pressure mercury lamp with a 365 nm band path filter. A JEOL JES-X320 instrument (Akishima, Japan) was used for the oxygen reduction reaction at $-150 \degree C$. UV irradiation was performed using a xenon lamp through a 365 nm band path filter. The samples were pre-evacuated at room temperature for 60 min on a vacuum line before the ESR measurements, and oxygen gas (1.0 Torr) was added to the ESR sample tube at 25 $\degree C$.

![Figure 8. Schematic of the (a) proposed reaction mechanism and (b) energy diagram for oxidative decomposition of acetic acid by Ti$^{3+}$-rich rutile TiO$_2$ photocatalysis.](image-url)
5. Conclusions

We investigated TiO$_2$ photocatalysts for the oxidative decomposition of acetic acid to CO$_2$ under UV and violet light irradiation. Rutile TiO$_2$ samples were prepared from Evonik TiO$_2$ P 25 through calcination at 800 °C, followed by H$_2$ treatment at 700 °C. H$_2$-treated TiO$_2$ exhibited high photocatalytic activity, which is comparable to highly active anatase TiO$_2$, despite its rutile structure and low specific surface area. The high photocatalytic activity under UV irradiation was due to the increase in Ti$^{3+}$ density and the improvement in charge separation, as confirmed by ESR. In the presence of O$_2$, anatase TiO$_2$ promoted the formation of O$_2^•−$ and O$_4^•−$; however, rutile TiO$_2$ did not exhibit an O$_2^•−$ signal. This is because the conduction band edge of rutile is not suitable for the one-electron reduction of oxygen. We observed that the two-electron reduction of O$_2$ to H$_2$O$_2$ was dominant in rutile TiO$_2$ photocatalysis, and the in situ-formed H$_2$O$_2$ accelerated the decomposition of acetic acid. We also found that Ti$^{3+}$-rich rutile TiO$_2$ can work even under violet light irradiation (wavelength = 405 nm) owing to its narrower $E_g$ (3.0 eV), and its intrinsic activity per unit surface area is significantly high. The apparent quantum efficiency of H$_2$-treated TiO$_2$ for CO$_2$ evolution was 4.9% at 405 nm, where conventional TiO$_2$ photocatalysts do not work efficiently.

**Supplementary Materials:** The full supporting information can be downloaded at [https://www.mdpi.com/article/10.3390/catal12101079/s1](https://www.mdpi.com/article/10.3390/catal12101079/s1). Figure S1: ESR spectrum of pure O$_2$ recorded at $−150$ °C.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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