Co-Catalytic Action of Faceted Non-Noble Metal Deposits on Titania Photocatalyst for Multielectron Oxygen Reduction

Peng Wang *,† and Bunsho Ohtani *

Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan
* Correspondence: peng.wang1@unsw.edu.au (P.W.); ohtani@cat.hokudai.ac.jp (B.O.)
† Present address: The University of New South Wales, Sydney 2052, Australia.

Received: 14 September 2020; Accepted: 30 September 2020; Published: 3 October 2020

Abstract: In order to clarify the reason of often reported low photocatalytic activity of rutile titania compared to that of anatase titania and the sluggish kinetics for oxygen reduction of rutile titania, in this study, faceted copper(I) oxide (Cu$_2$O) particles (FCPs), i.e., cube, cuboctahedron and octahedron, were deposited onto rutile particles by an in-situ wet chemical method, and the co-catalytic action of FCPs was studied in the oxidative decomposition of acetic acid. The oxygen reduction reaction kinetics of bare and FCP-loaded titania samples in photodecomposition of organic compounds were investigated by light-intensity dependence measurement. FCPs serve as the specific sites (sink) which accumulate excited electrons to drive multielectron oxygen reduction reactions, as the counter reaction in photodecomposition of organic compounds by positive holes, which significantly improves the photocatalytic activity of rutile titania particles.

Keywords: photocatalyst; co-catalytic action; multielectron oxygen reduction; titania

1. Introduction

The application of photocatalysis technology has merged as a possible facile and scalable strategy for processing organic wastes using sunlight, where both oxidative decomposition of organic contaminants and reduction of oxygen occur spontaneously on the surface of semiconductor catalysts. Over the past decades, titania has been considered as one of the most promising semiconductor photocatalysts for photocatalytic degradation of organic compounds, due to its abundance, low cost and high chemical stability [1–4]. However, the large bandgap of titania (3.0–3.2 eV) restricts its light absorption to the ultraviolet (UV) region, which only takes 3–5% in energy of the whole solar spectrum. Some researchers have made various attempts to narrow the bandgap of titania by doping sulphur, nitrogen, and copper etc [5–7]. The frequently reported low photocatalytic activity of rutile titania might be attributed to its lower ability to drive oxygen reduction due to a slightly lower conduction-band bottom (CBB) energy for driving one-electron reduction of oxygen. However, sluggish kinetics for oxygen reduction have rarely been attempted yet remain crucial for the development of organics degradation photocatalysts. Copper(I) oxide (Cu$_2$O) is promising co-catalyst for rutile titania in the photodecomposition of organic compounds, due to its non-toxicity, earth-abundance, visible-light activity and more importantly, the effective adsorption of oxygen molecules, which scavenges the photogenerated electrons to suppress the recombination of electron-hole pairs and promotes photocatalytic activity [8–10]. Faceted particles with different crystallographic features could be synthesized by controlled facets growth and have been reported to demonstrate diverse properties in sensing and catalysis [11–14]. Unfortunately, to date, the co-catalytic activity of faceted Cu$_2$O particles has remained veiled. In addition, despite the fact that photocatalysts and their photocatalytic activities...
are always the focus in the literature, research on the mechanism of reactions on the photocatalyst surface, especially the half-reaction of oxygen reduction, has rarely been attempted. Thus, this research focused on the fundamental investigation of co-catalytic action of faceted Cu$_2$O particles and the oxygen reduction reaction, especially multielectron oxygen reduction, during the decomposition of dissolved organic contaminants.

2. Results and Discussion

As shown in Figure 1, with addition of a polyvinylpyrrolidone (PVP) modifier, the shape of Cu$_2$O was successfully altered from cube to cuboctahedron and octahedron due to the preferential absorption to the [111] planes of the Cu$_2$O crystals [15]. Samples are denoted as c, co and o. The exposed surfaces of cube, cuboctahedron and octahedron were composed of six [100] facets, eight [111] facets and six [100] facets, and eight [111] facets, respectively. The size of particles was in the range of 600–800 nm. The PVP with higher molecular weight was more beneficial for the shape transformation from octahedron to cuboctahedron. PVP is a non-ionic surfactant, and an easily polarized functional group—C=O is included in its repetition unit. For a polymer, the length of the molecular chain is proportional to its molecular weight. With higher molecular weight of PVP, the absorption dots to Cu$_2$O particles would decrease due to the space restriction, which would in turn decrease the ratio of {111}/{100} [15–17]. As shown in Figure 1, when the molecular weight of PVP increased from 29,000 to 40,000, the shape of Cu$_2$O changed from octahedron to cuboctahedron.

![Figure 1. SEM images of faceted Cu$_2$O particles (FCPs) synthesized at 328 K (a–c) and room temperature (d–f). (a) cube (c), (b) cuboctahedron (co), (c) octahedron (o), (d) r-c, (e) r-co and (f) r-o. The size distribution histograms for r-c, r-co and r-o are inserted.](image)

The co-catalytic activity of the deposits highly depends on its particle size. Generally speaking, deposits with smaller particle size show higher specific surface area, and high photocatalytic activity can be expected. The prepared Cu$_2$O with such a large particle size (600–800 nm) might not be good for its catalytic activity, thus Cu$_2$O with much smaller particle size was synthesized at room temperature, denoted as r-c, r-co and r-o. Although it was a little challenging to obtain very high resolution images with clear edges, due to the small size of particles and resolution limitation of the SEM equipment, morphology evolution of faceted Cu$_2$O particles (FCPs) could still be observed from cube (only [100] facets) to cuboctahedron (coexist of [100] and [111] facets) and octahedron (only [111] facets), with preferential absorption of PVP modifier to the [111] planes of the Cu$_2$O crystals. High reaction temperature was beneficial for the fast growth of the particles, thus particles with bigger size were formed at 328 K. On the contrary, when reaction of Cu$_2$O occurred at room
temperature, FCPs with much smaller size (70–130 nm) could be synthesized as shown in the inserted size distribution histograms.

As expected, no peaks of CuO or Cu were detected in the XRD patterns in Figure 2. Only peaks attributed to Cu$_2$O were observed. This indicates the successful synthesis of Cu$_2$O without other crystalline contaminants. Peaks located at 29.6°, 36.5°, 42.4° and 52.5° are attributed to the [110], [111], [200] and [211] facets of Cu$_2$O, respectively.

As shown in Figure 3, cuboctahedron Cu$_2$O showed the highest CO$_2$ evolution rate, followed by octahedron and cube. Some researchers found that the {111} facet is more photocatalytically active than the {100} facet, due to the fact that the surface energy of the {100} facet was lower than that of the {111} facet. Thus, it is expected that cubic Cu$_2$O with six exposed {100} facets had lower photocatalytic activity than octahedron Cu$_2$O with eight exposed {111} facets. In cuboctahedron Cu$_2$O, eight {111} facets and six {100} facets are exposed. A possible explanation is that the energy difference in the {100} and {111} facets allows better charge separation and transfer, thus electron-hole recombination can be suppressed. Therefore, a higher photocatalytic activity is obtained for the cuboctahedron compared to the cube and octahedron. It is worthwhile to note that the photoactivity of Cu$_2$O nanoparticles was much lower than that of ST-G2 (mainly rutile titania). The reason might be that Cu$_2$O could react with acetic acid into copper(II) ions, which could reduce its photocatalytic activity. This is evidenced by the color change of the reaction solution which ended up with a slightly blueish color after the photocatalytic activity measurement. Thus, co-catalytic activity of FCP-loaded ST-G2 is discussed in the following section.

FCP-loaded titania was prepared by in-situ wet chemical method at room temperature, denoted as r-c-S, r-co-S and r-o-S. The theoretical loading amount of faceted Cu$_2$O particles was 2 wt%. Faceted Cu$_2$O particles with shapes of cube, cuboctahedron and octahedron can be observed in SEM images in Figure 4. The shape evolution of faceted Cu$_2$O particles can be better observed for FCP-loaded titania synthesized at 328 K (See Figure S1). The density of FCPs is low, due to the low loading amount of faceted Cu$_2$O particles. Other particles are attributed to ST-G2 titania particles. It seemed that faceted Cu$_2$O particles were well-interacted with titania particles due to the in-situ wet chemical method. Elemental mapping and EDS analyses were also performed for titania and FCP-loaded titania (See Figures S2 and S3). EDS results showed that no peaks of copper element were detected on bare ST-G2 powder. On the other hand, a peak with energy of 0.930 keV was observed for all FCP-loaded ST-G2 composites (c-S, co-S and o-S). This implies that Cu$_2$O was successfully loaded onto ST-G2 particles by the wet chemical synthesis, which is in good agreement with XRD patterns.

![Figure 2. XRD patterns of faceted Cu$_2$O particles (FCPs).](image-url)
Catalysts 2020, 10, x FOR PEER REVIEW 4 of 13

Figure 3. Photocatalytic activity PCFs in a CO2 system. FCP-loaded titania was prepared by in-situ wet chemical method at room temperature, denoted as r-c-S, r-co-S and r-o-S. The theoretical loading amount of faceted Cu2O particles was 2wt%. Faceted Cu2O particles with shapes of cube, cuboctahedron and octahedron can be observed in SEM images in Figure 4. The shape evolution of faceted Cu2O particles can be better observed for FCP-loaded titania synthesized at 328 K (See Figure S1). The density of FCPs is low, due to the low loading amount of faceted Cu2O particles. Other particles are attributed to ST-G2 titania particles. It seemed that faceted Cu2O particles were well-interacted with titania particles due to the in-situ wet chemical method. Elemental mapping and EDS analyses were also performed for titania and FCP-loaded titania (See Figures S2 and S3). EDS results showed that no peaks of copper element were detected on bare ST-G2 powder. On the other hand, a peak with energy of 0.930 keV was observed for all FCP-loaded ST-G2 composites (c-S, co-S and o-S). This implies that Cu2O was successfully loaded onto ST-G2 particles by the wet chemical synthesis, which is in good agreement with XRD patterns.

Figure 4. SEM images of titania and FCP-loaded titania. Enlarged SEM images are inserted. Figure 5 shows that no peaks of CuO, Cu or other contaminants were detected in the XRD patterns. Peaks located at 27.7°, 36.3° and 54.8° in Figure 5b are assigned to the {110}, {101} and {211} planes of rutile titania, respectively. Peaks at 25.4° and 48.16° are the characteristic peaks for anatase titania with planes of {101} and {200}, respectively. The XRD results confirmed the composition of ST-G2, including approximately 97% of rutile and 3% anatase titania; ST-G2 is mainly composed of the rutile phase with small amount of anatase. The particle size of ST-G2 is large, approximately 500 nm. In terms of in-situ synthesized FCP-loaded titania composites, Figure 5a shows that new peaks located at 36.5°
and 42.4° were observed, which are attributed to the [111] and [200] planes of Cu₂O. This was also in good agreement with XRD patterns of FCP-loaded titania synthesized at 328 K (See Figure S4). This implies the successful loading of FCP deposits onto ST-G2 by wet chemical synthesis.

![Figure 5. XRD patterns of titania (ST-G2) and FCP-loaded titania. (a) is the zoomed-in XRD patterns between 25° to 45°, (b) are the [110], [101] and [211] planes of rutile titania, respectively.](image)

Figure 6 shows that ST-G2 titania (mainly rutile) can absorb light with wavelengths longer than 420 nm, due to its large bandgap. The loading of FCPs could extend the light absorption of ST-G2 to the visible-light range. Thus, the FCP-loaded titania showed much higher absorption than that of bare titania. It is consistent with the results of FCP-loaded titania synthesized at 328 K (See Figure S5). As it has been reported that titania is one of the most promising photocatalysts due to its high chemical stability, sufficient energy to drive various photocatalytic reactions and inexpensiveness, despite that only ultraviolet light can be absorbed due to its large bandgap (3.0–3.2 eV). The deposition of FCPs on titania can be a promising and facile method to extend the light absorption of titania to utilize visible light in the whole light spectrum.

![Figure 6. (a) Diffuse reflectance spectra and (b) Tauc plots with Kubelka–Munk function derived from reflection spectra of titania (ST-G2) and FCP-loaded titania.](image)

The Kubelka–Munk function derived from reflection spectra shows that the calculated bandgap of ST-G2 was 3.05 eV, which is comparable to the reported value of 3.0 eV. In terms of the FCP-loaded ST-G2, two components could be seen in the Tauc plot in Figure 6b. The calculated bandgap of Cu₂O was 2.0 eV, which agrees well with reported bandgap of 2.0–2.2 eV [18,19]. Taking into account of SEM, XRD and diffuse reflectance spectroscopy (DRS), it can be concluded that FCP-loaded ST-G2 was...
successfully synthesized by the wet chemical method, and the synthesized composites may be visible light-active photocatalysts.

In order to understand the co-catalytic action of FCP deposits on titania, photocatalytic activity of titania (ST-G2) and FCP-loaded titania was examined in a CO$_2$ system. Figure 7a shows that FCP-loaded titania showed much higher photocatalytic activity than that of bare titania, suggesting the role of FCPs as an electron sink, which helps accumulation of electrons to drive oxygen reduction reactions. The photocatalytic activity of FCP-loaded titania decreased in the sequence of cube > cuboctahedron > octahedron, due to the preferable electron transfer from titania to [100] facets rather than [111] facets of FCPs. It is worthwhile to note that the r-c-S showed photocatalytic activity seven times as high as the that of bare ST-G2, implying the role of FCPs in suppressing electron-hole recombination and accelerating electrons diffusion from titania to FCPs due to the difference of electron concentration under UV-light illumination.

As shown in Figure 8a, since the CBB of anatase titania has been reported to be 0.20V more positive than that of bare titania, much enhanced photocatalytic activity was observed for the sample r-c-S. This indicates that good interaction between Cu$_2$O and titania was achieved by the in-situ wet chemical synthesis, which may lead to fast electron transfer between particles [20]. In addition, it is interesting to find that the r-c-S sample also showed higher photocatalytic activity than that of (noble metal) Pt-loaded titania. This can be explained by several aspects: (1) The Cu$_2$O particles serve as an electron sink to accumulate photogenerated electrons from titania, which can be consumed to drive the oxygen reduction reaction. (2) The [100] facet of Cu$_2$O particles is the most active facet to favourably accumulate electrons transferred from titania. (3) Cu$_2$O has a higher ability of molecular-oxygen adsorption, which allows quick consumption of accumulated electrons and suppression of electron-hole recombination. (4) The possible multielectron oxygen reduction occurs as the counter reaction of the photodecomposition of organic compounds.

As shown in Figure 8a, since the CBB of anatase titania has been reported to be 0.20V more negative than the standard electrode potential of one-electron oxygen reduction, one-electron oxygen reduction takes place. On the other hand, the CBB of rutile titania is a little more positive than the one-electron oxygen reduction potential, thus two-electron reduction of oxygen occurs [21]. Therefore, it is considered that two-electron reduction of oxygen may occur in rutile titania and one-electron reduction of oxygen in anatase titania. A sample ST-G2 (Showa Denko Ceramics) is composed of mainly rutile and a small portion of anatase, while the other sample FP6 (Showa Denko Ceramics) is composed of mainly anatase and a small portion of rutile. The photocatalytic activity of ST-G2 was much lower than that of FP6, due to the lower CBB position to drive one-electron reduction of oxygen and absence of surface/bulk sites to accumulate excited electrons to drive multielectron oxygen reduction reactions.
Figure 8. (a) Schematic diagram of possible oxygen reduction reactions of titania and (b) light-intensity dependence (LID) of photocatalytic activities of titania (ST-G2, blue) and FCP-loaded titania (r-c-S, red).

The oxygen reduction reaction kinetics of bare titania (ST-G2) and FCP-loaded titania (r-c-S) in photodecomposition of organic compounds were investigated by the light-intensity dependence (LID) measurement under UV-LED (365 nm) irradiation, on the assumption that (i) only the titania particles with accumulated two electrons can reduce oxygen without deactivation. In this scheme, if the one-electron bearing particles cannot absorb the second photon, they are deactivated leading to no chemical reactions. (ii) Organics decomposition proceeds through peroxy radical-mediated radical chain reaction. Since the CBB of rutile titania is slightly more positive than the standard electrode potential of one-electron reduction of oxygen, multielectron (two or four) oxygen reduction (MOR) might occur [22–25].

Then, a kinetic model was used to analyze LID. The following reaction steps involving titania (<TiO$_2$>, one electron-bearing titania (<TiO$_2$(e$^-$)>, two electron-bearing titania (<TiO$_2$(e$^-$)>, reaction substrate (RH), peroxy radical chain carrier (RO$_2$.), hydroperoxide (RO$_2$H) and its dimer (RO$_4$R), are assumed.

\begin{align}
\text{<TiO}_2 + \text{hv} &\rightarrow \text{<TiO}_2(e^-) \quad I\psi_0\phi \\
\text{<TiO}_2(e^-) &\rightarrow \text{<TiO}_2 \quad 1/\tau_1[\text{TiO}_2(e^-)] \\
\text{<TiO}_2(e^-) + \text{hv} &\rightarrow \text{<TiO}_2(e^- e^-) \quad I\psi_1\phi[\text{TiO}_2(e^-)] \\
\text{<TiO}_2(e^- e^-) &\rightarrow \text{<TiO}_2 \quad 1/\tau_2[\text{TiO}_2(e^- e^-)] \\
\text{<TiO}_2(e^- e^-) + \text{RH} &\rightarrow \text{<TiO}_2 + \text{R} \quad k[\text{TiO}_2(e^- e^-)][\text{RH}] \\
\text{R} + \text{O}_2 &\rightarrow \text{RO}_2. \quad k_1[\text{R}][\text{O}_2] \\
\text{RO}_2. + \text{RH} &\rightarrow \text{RO}_2\text{H} + \text{R} \quad k_p[\text{RO}_2.][\text{RH}] \\
2\text{RO}_2. &\rightarrow \text{RO}_4\text{R} \quad k_4[\text{RO}_2.]^2
\end{align}

where \( I, \psi_0, \psi_1, \phi \) and \( k \)'s are light intensity, absorption efficiency of \(<\text{TiO}_2>\), absorption efficiency of \(<\text{TiO}_2(e^-)>\), quantum efficiency of charge separation and rate constants, respectively. In this model, photodegradation of RH starts only by \(<\text{TiO}_2(e^- e^-)>\), i.e., two-photon absorption is necessary as is autooxidation, a radical-chain reaction by the RO$_2.$ chain carrier. The efficiency of excitation to create an electron-positive hole pair, \( \psi_0 \), can be assumed to be the same for \(<\text{TiO}_2>\) and \(<\text{TiO}_2(e^-)>,\) since the efficiency depends predominantly on the properties of titania, while photoabsorption coefficients, \( \psi_0 \) and \( \psi_1 \), may be different, since \( \psi_0 \) depends predominantly on the bulk composition, i.e., the photoabsorption coefficient of titania, but \( \psi_1 \) must depend also on the effective size of a particle, as discussed later.
By applying steady-state approximation to \(<\text{TiO}_2(e^-)>, <\text{TiO}_2(e^-)>\), R\(\cdot\) and RO\(\cdot\)· (d[\text{TiO}_2(e^-)])/dt = d[R\cdot]/dt = d[RO\cdot]/dt = 0), the following equations are derived.

\[
[\text{TiO}_2(e^-)] = \psi_0 \varphi / (1/\tau_1 + \psi_1 \varphi) \tag{9}
\]
\[
[\text{TiO}_2(e^-)] = \psi_0 \varphi / (1/\tau_1 + \psi_1 \varphi) \tag{10}
\]
\[
[R\cdot]: \{k[\text{TiO}_2(e^-)][\text{RH}] + k_p[\text{RO}_2\cdot][\text{RH}] \} = k[R\cdot][\text{O}_2] \tag{11}
\]
\[
[\text{RO}_2\cdot]: k\{k[\text{RO}_2\cdot][\text{RH}] + k_i[\text{RO}_2]\} \tag{12}
\]

Concentrations of \(<\text{TiO}_2(e^-)>, <\text{TiO}_2(e^-)>\) and RO\(\cdot\) are obtained from Equations (9) and (10) as:

\[
[\text{TiO}_2(e^-)] = \psi_0 \varphi / (1/\tau_1 + \psi_1 \varphi) \tag{13}
\]
\[
[\text{TiO}_2(e^-)] = \psi_0 \varphi / (1/\tau_1 + \psi_1 \varphi) \tag{14}
\]
\[
I^2 \psi_0 \psi_1 \varphi^2 / (1/\tau_1 + \psi_1 \varphi) (1 + 1/k[\text{RH}] \tau_2) = k_i[\text{RO}_2]\tag{15}
\]
\[
[\text{RO}_2\cdot] = [I^2 \psi_0 \psi_1 \varphi^2 / (k_1 (1/\tau_1 + \psi_1 \varphi) (1 + 1/k[\text{RH}] \tau_2))]^{1/2} \tag{16}
\]

Then, overall rate (r) is obtained as,

\[
r = -d[\text{RH}]/dt = k[\text{TiO}_2(e^-)][\text{RH}] + k_p[\text{RO}_2\cdot][\text{RH}]
\]
\[
k[\text{RH}] I^2 \psi_0 \psi_1 \varphi^2 / (1/\tau_1 + \psi_1 \varphi) (k[\text{RH}] + 1/\tau_2)
\]
\[
+ k_p[\text{RH}][I^2 \psi_0 \psi_1 \varphi^2 / (k_1 (1/\tau_1 + \psi_1 \varphi) (1 + 1/k[\text{RH}] \tau_2)))]^{1/2} \tag{17}
\]
\[
ar \psi_0 \psi_1 \varphi^2 I^2 / (1 + \psi_1 \varphi \tau_1) + k_p[\text{RH}] (ar \psi_0 \psi_1 \varphi^2 I^2 / k_1 (1 + \psi_1 \varphi \tau_1))^{1/2},
\]

where \(a = 1/(\tau_1 (1 + 1/k[\text{RH}] \tau_2))\). Assuming sufficiently high chain length of the second-term radical chain to be able to neglect the first term in Equation (17), the LID of rate \(r\) can be of the first and 0.5th-order at the low and high limit of light intensity, \(l\) [17]. At the low and high limit of light intensity, \(l\), the rates are:

\[
r(\text{low}) = k_p[\text{RH}] (ar \psi_0 \psi_1 \varphi^2 I^2 / k_1)^{1/2} = bl \tag{18}
\]
\[
r(\text{high}) = k_p[\text{RH}] (ar \psi_0 \varphi I / k_1 \tau_1)^{1/2} = bc l^{1/2}, \tag{19}
\]

where, \(b\) and \(c\) correspond to \(k_p[\text{RH}] (ar \psi_0 \psi_1 \varphi^2 / k_1)^{1/2}\) and \((1/\psi_1 \varphi \tau_1)^{1/2}\), respectively. The presumed bimodal LID was observed for bare ST-G2 (Figure 8). The first-order dependence is interpreted by the fact that, at lower light intensity, the probability of accumulation of two electrons, i.e., absorption of two photons in a photocatalyst particle, is low and LID of this event should be second order to lead to first order LID of the overall rate by multiplication of 0.5th-order LID of the following radical chain reaction. At the higher light intensity, the probability of two-photon absorption is sufficiently high to make the LID of two-electron accumulation first order to result in 0.5th order overall-rate LID.

By loading FCPs on ST-G2, the activity was much enhanced, i.e., LID was shifted upward as shown in Figure 8. The inflection point of the first and 0.5th-order LID observed at ca. 2.5 (ln \(l\)) and the first-order LID could not be seen when r-c-S was used as a photocatalyst. Since \(r(\text{low}) = r(\text{high})\) at the inflection point, \(l_{\text{thr}}\), \(l_{\text{thr}}\) is calculated to be 1/\(\psi_1 \varphi \tau_1\). Photoabsorption efficiency of \(<\text{TiO}_2(e^-)>, \psi_1\), depends on the size of particles; the larger the size is, the higher becomes the probability of absorbing a second photon to be \(<\text{TiO}_2(e^-)>, \psi_1\), and therefore it is assumed that \(\psi_1\) is constant for particles with or without FCPs. These results suggested that loading of FCPs on titania promoted the charge separation (\(\varphi\)) and/or extended the lifetime of \(<\text{TiO}_2(e^-)>\) to reduce \(l_{\text{thr}}\) and overall reaction rate, most probably by capturing electron(s). At the further lowered light intensity, the overall rate was markedly low enough not to be determined precisely.

Another feature of LID of photocatalytic activity of r-c-S. The rage became almost constant, i.e., zero-order LID was observed at ca. In \(l = 3\). Although this cannot be explained in the above-mentioned
kinetic model, the reaction step of two electron-bearing titania (Equation (5)) requires the presence of oxygen to accept those electrons. At the higher intensity region, concentration of oxygen near the surface of FCP particles might become very low or even almost zero and thereby the overall reaction rate might be oxygen-diffusion limited. At the further higher intensity, the overall rate was increased again with the increase in light intensity. Since the diffusion of oxygen to the surface of FCP deposits have been already limited, such increase in the overall rate must be induced by oxygen reduction, presumably four-electron process, on the surface of titania, but not on FCPs. In such a case, LID of photoabsorption and overall rate may be fourth order and second order, respectively, and this seems consistent with the results shown in Figure 8.

3. Materials and Methods

3.1. Material Preparation

All of the chemical reagents used in this experiment were of analytical grade and used without further purification.

In a typical synthesis, given amounts of polyvinylpyrrolidone (PVP; 0 g, 3.333 g (MW 40,000), or 3.333 g (MW 29,000), Sigma-Aldrich, St Louis, MO, USA) were dissolved into a 100-mL aqueous solution of copper(II) chloride (CuCl$_2$; 0.01 mol L$^{-1}$, Wako Pure Chemical Industries, Osaka, Japan). Then, a 10.0-mL aqueous sodium hydroxide (NaOH, Wako Pure Chemical Industries, Osaka, Japan) solution (2.0 mol L$^{-1}$) was added into the above-mentioned transparent solution. Then a 10-mL ascorbic-acid solution (0.6 mol L$^{-1}$, Wako Pure Chemical Industries, Osaka, Japan) was added dropwise into the mixture. The mixture was aged for 3 h. Samples synthesized at a given temperature of 328 K are denoted as “c”, “co” and “o”, while samples synthesized by the identical process at room temperature (298 K) are denoted as “r-c”, “r-co” and “r-o”. The resulting precipitate was collected by centrifugation, followed by washing with distilled water and absolute ethanol, and finally dried in vacuum at 333 K for 5 h for further characterization.

In a typical synthesis, a 1.764-g portion of titania (ST-G2, Showa Denko Ceramics, Toyama, Japan, size: 500 nm) powder was suspended in a 50.0-mL aqueous solution of CuCl$_2$ (0.01 mol L$^{-1}$). The theoretical loading amount of faceted Cu$_2$O particles was 2 wt%. Given amounts of PVP (0 g, 1.6665 g (MW 40,000), or 1.6665 g (MW 29,000)) were dissolved into the suspension. Then, 5.0-mL aqueous NaOH solution (2.0 mol L$^{-1}$) was added into the suspension. Then a 5-mL ascorbic acid-solution (0.6 mol L$^{-1}$) was added dropwise into the suspension. The mixture was aged for 3 h. Samples synthesized in a water bath at a given temperature of 328 K are denoted as “c-S”, “co-S” and “o-S”, while samples synthesized by the identical process at room temperature (298 K) are denoted as “r-c-S”, “r-co-S” and “r-o-S”. The resulting precipitate was collected by centrifugation, followed by washing with distilled water and absolute ethanol, and finally dried in vacuum at 333 K for 5 h for further characterization.

The photodeposition method was used to deposit platinum on titania (ST-G2), where the identical method developed by our group was followed [26]. A 600-mg portion of the titania was suspended in 28.6 mL of 50 vol% aqueous methanol. Hexachloroplatinic acid (Wako Pure Chemical Industries, Osaka, Japan) was dropwise added into the suspension to make platinum (Pt) deposited on titania during photoirradiation. The loading amount of Pt was maintained to be 2 wt%. The obtained Pt-loaded titania were denoted as “Pt-S”. The suspension was purged of air with argon for 10 min in a test tube. A 400-W high-pressure mercury lamp (Eiko-sha, Tokyo, Japan) under thermostatic control at room temperature was used as an irradiation light source. The amount of evolved hydrogen (H$_2$) was measured by gas chromatography—thermal conductivity detector (GC-TCD, Shimadzu, Kyoto, Japan). For comparison, bare commercial copper(I) oxide (Wako Pure Chemical Industries, Osaka, Japan) was physically mixed with titania (ST-G2) in an agate mortar, denoted as “b-S”, and the loading amount of bare copper (I) oxide was 2 wt%.
3.2. Material Characterizations

The morphology was characterized by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-7400F, JEOL, Tokyo, Japan). The elemental analysis of synthesized materials was performed by energy-dispersive X-ray spectroscopy (EDS, equipped in the FE-SEM, JED-2300, JEOL, Tokyo, Japan). The phase composition and crystallinity were measured by X-ray diffraction (XRD, Rigaku, Tokyo, Japan). Powder X-ray diffraction (XRD) analysis was performed using a Rigaku SmartLab diffractometer equipped with a sealed tube X-ray generator (a copper target; operated at 40 kV and 30 mA), a D/teX high-speed position-sensitive detector system and an ASC-10 automatic sample changer. All of the XRD measurements were performed under the following conditions: 2θ range, 10°–90°; scan speed, 1.00° min⁻¹; and scan step, 0.008°. The obtained XRD patterns were analyzed by Rigaku PDXL software (Rigaku, Tokyo, Japan), including the Rietveld analysis package, installed in a computer controlling the diffractometer. The optical property of synthesized materials was measured by diffuse reflectance spectroscopy (DRS, JASCO V-670 spectrophotometer equipped with a PIN-757 integrating sphere, JASCO, Tokyo, Japan) with barium sulfate as a reference.

3.3. Photocatalytic Activity Measurement

Photocatalytic activities of prepared photocatalysts were examined for photocatalytic carbon-dioxide (CO₂) liberation by oxidative decomposition of acetic acid. A 50-mg portion of a photocatalyst was suspended in a 5-mL 5.0vol% aqueous acetic-acid solution (Wako Pure Chemical Industries, Osaka, Japan) and irradiated with a 400-W high-pressure mercury lamp under vigorous magnetic stirring (1000 rpm). The amount of liberated CO₂ gas was measured by gas chromatography—thermal conductivity detector (GC-TCD, Shimadzu, Kyoto, Japan). Light-intensity dependence was measured in the CO₂ system using 30 mg of sample powder suspended in 3-mL of 5.0vol% aqueous acetic-acid solution. A UV-LED emitting light of wavelength of 365 nm (NS Lighting ULDEN101, NS Lighting, Tokyo, Japan) was used as the illumination source, and the light-intensity dependence of the rate of CO₂ liberation was measured.

4. Conclusions

Faceted Cu₂O particles (FCPs), i.e., cubes exposing six [100] facets, cuboctahedrons exposing eight [111] and six [100] facets, and octahedrons exposing eight [111] facets, were synthesized by adjusting the PVP modifier during the formation of Cu₂O particles. FCPs were loaded onto titania by an in-situ wet chemical method. The photoabsorption of titania was extended to the visible light region with the assistance of FCPs. The co-catalytic action study of FCPs showed that the [100] facet of Cu₂O particles is the most active facet to favourably accumulate electrons transferred from titania. FCPs could serve as electron sinks to help accumulate electrons to drive multielectron oxygen reduction reactions, thus, rutile titania can be activated even though it may have lower (less energy) CBB to drive one-electron oxygen reduction. Multielectron oxygen reduction, as a counter reaction in photodecomposition of organic compounds, accounted for the enhanced photocatalytic activity of FCP-loaded titania composites.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/10/1145/s1, Figure S1: SEM images of titania and FCP-loaded titania synthesized at 328 K, Figure S2: SEM images and EDS mapping results of o-S, Figure S3: EDS spectra of titania and FCP-loaded titania synthesized at 328 K, Figure S4: XRD patterns of titania (ST-G2) and FCP-loaded titania. (a) Is the zoom-in XRD patterns between 25° to 45°, Figure S5: (a) Diffuse reflectance spectra and (b) Tauc plots with Kubelka–Munk function derived from reflection spectra of titania (ST-G2) and FCP-loaded titania.

Author Contributions: Methodology, investigation, writing—original draft, P.W.; Writing—review and editing, B.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partly funded by Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship Program for Overseas Researchers (grant number 16001524).
Acknowledgments: Financial support from Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship Program for Overseas Researchers is acknowledged.

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

References

1. Fujishima, A.; Zhang, X.; Tryk, D.A. TiO2 photocatalysis and related surface phenomena. Surf. Sci. Rep. 2008, 63, 515–582. [CrossRef]
2. Nakata, K.; Fujishima, A. TiO2 photocatalysis: Design and applications. J. Photochem. Photobiol. C 2012, 13, 169–189. [CrossRef]
3. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO2 photocatalysis: Mechanisms and materials. Chem. Rev. 2014, 114, 9919–9986. [CrossRef] [PubMed]
4. Rej, S.; Mascaretti, L.; Santiago, E.Y.; Tomanec, O.; Kment, Š.; Wang, Z.; Zbořil, R.; Fornasiero, P.; Govorov, A.O.; Naldoni, A. Determining Plasmonic Hot Electrons and Photothermal Effects during H2 Evolution with TiN–Pt Nanohybrids. ACS Catal. 2020, 10, 5261–5271. [CrossRef]
5. Emeline, A.V.; Kuznetsov, V.N.; Rybchuk, V.K.; Serpone, N. Visible-Light-Active Titania Photocatalysts: The Case of N-Doped TiO2s—Properties and Some Fundamental Issues. Int. J. Photoenergy 2008, 2008, 258394. [CrossRef]
6. Umebayashi, T.; Yamaki, T.; Itoh, H.; Asai, K. Band gap narrowing of titanium dioxide by sulfur doping. Appl. Phys. Lett. 2002, 81, 454–456. [CrossRef]
7. Assadi, M.H.N.; Hanaor, D.A.H. The effects of copper doping on photocatalytic activity at (101) planes of anatase TiO2: A theoretical study. Appl. Surf. Sci. 2016, 387, 682–689. [CrossRef]
8. Marschall, R. Semiconductor Composites: Strategies for Enhancing Charge Carrier Separation to Improve Photocatalytic Activity. Adv. Funct. Mater. 2013, 24, 2421–2440. [CrossRef]
9. Xu, X.; Gao, Z.; Cui, Z.; Liang, Y.; Li, Z.; Zhu, S.; Yang, X.; Ma, J. Synthesis of Cu2O Octadecahedron/TiO2 Quantum Dot Heterojunctions with High Visible Light Photocatalytic Activity and High Stability. ACS Appl. Mater. Interfaces 2016, 8, 91–101. [CrossRef]
10. Wei, T.; Zhu, Y.-N.; An, X.; Liu, L.-M.; Cao, X.; Liu, H.; Qu, J. Defect Modulation of Z-Scheme TiO2/Cu2O Photocatalysts for Durable Water Splitting. ACS Catal. 2019, 9, 8346–8354. [CrossRef]
11. Shang, Y.; Guo, L. Facet-Controlled Synthetic Strategy of Cu2O-Based Crystals for Catalysis and Sensing. Adv. Sci. 2015, 2, 1500140. [CrossRef]
12. Esmat, M.; Farghali, A.A.; El-Dek, S.I.; Khedr, M.H.; Yamauchi, Y.; Bando, Y.; Fukuta, N.; Ide, Y. Conversion of a 2D Lepidocrocite-Type Layered Titanate into Its 1D Nanowire Form with Enhancement of Cation Exchange and Photocatalytic Performance. Inorg. Chem. 2019, 58, 7989–7996. [CrossRef] [PubMed]
13. Doustkhal, E.; Najafi Zare, R.; Yamauchi, Y.; Tabei-Kafrawi, A.; Mohtasham, H.; Esmat, M.; Ide, Y.; Fukuta, N.; Rostamnia, S.; Sadeghi, M.H.; et al. Template-oriented synthesis of hydroxyapatite nanofibers for 3D bone printing. J. Mater. Chem. B 2019, 7, 7228–7234. [CrossRef] [PubMed]
14. Wang, P.; Ng, Y.H.; Amal, R. Embedment of anodized p-type Cu2O thin films with CuO nanowires for improvement in photoelectrochemical stability. Nanoscale 2013, 5, 2952–2958. [CrossRef] [PubMed]
15. Zhang, D.-F.; Zhang, H.; Guo, L.; Zheng, K.; Han, X.-D.; Zhang, Z. Delicate control of crystallographic facet-oriented Cu2O nanocrystals and the correlated adsorption ability. J. Mater. Chem. 2009, 19, 5220–5225. [CrossRef]
16. Liang, X.; Gao, L.; Yang, S.; Sun, J. Facile Synthesis and Shape Evolution of Single-Crystal Cuprous Oxide. Adv. Mater. 2009, 21, 2068–2071. [CrossRef]
17. Zhang, X.; Xie, Y.; Xu, F.; Liu, X.; Xu, D. Shape-controlled synthesis of submicro-sized cuprous oxide octahedra. Inorg. Chem. Commun. 2003, 6, 1390–1392. [CrossRef]
18. Handoko, A.D.; Tang, J. Controllable proton and CO2 photoreduction over Cu2O with various morphologies. Int. J. Hydrog. Energy 2013, 38, 13017–13022. [CrossRef]
19. Raebiger, H.; Lany, S.; Zunger, A. Origins of the p-type nature and cation deficiency in Cu2O and related materials. Phys. Rev. B 2007, 76, 045209. [CrossRef]
20. Liu, L.; Yang, W.; Sun, W.; Li, Q.; Shang, J.K. Creation of Cu2O@TiO2 Composite Photocatalysts with p–n Heterojunctions Formed on Exposed Cu2O Facets, Their Energy Band Alignment Study, and Their Enhanced Photocatalytic Activity under Illumination with Visible Light. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1465–1476. [CrossRef]

21. Prieto-Mahaney, O.-O.; Murakami, N.; Abe, R.; Ohtani, B. Correlation between Photocatalytic Activities and Structural and Physical Properties of Titanium(IV) Oxide Powders. *Chem. Lett.* **2009**, *38*, 238–239. [CrossRef]

22. Irie, H.; Miura, S.; Kamiya, K.; Hashimoto, K. Efficient visible light-sensitive photocatalysts: Grafting Cu(II) ions onto TiO2 and WO3 photocatalysts. *Chem. Phys. Lett.* **2008**, *457*, 202–205. [CrossRef]

23. Miyauchi, M.; Irie, H.; Liu, M.; Qiu, X.; Yu, H.; Sunada, K.; Hashimoto, K. Visible-Light-Sensitive Photocatalysts: Nanocluster-Grafted Titanium Dioxide for Indoor Environmental Remediation. *J. Phys. Chem. Lett.* **2016**, *7*, 75–84. [CrossRef] [PubMed]

24. Hori, H.; Takashima, M.; Takase, M.; Ohtani, B. Pristine Bismuth-tungstate Photocatalyst Particles Driving Organics Decomposition through Multielectron Reduction of Oxygen. *Chem. Lett.* **2017**, *46*. [CrossRef]

25. Hori, H.; Takashima, M.; Takase, M.; Ohtani, B. Kinetic analysis supporting multielectron reduction of oxygen in bismuth tungstate-photocatalyzed oxidation of organic compounds. *Catal. Today* **2018**, *313*, 218–223. [CrossRef]

26. Ohtani, B.; Iwai, K.; Nishimoto, S.-I.; Sato, S. Role of Platinum Deposits on Titanium(IV) Oxide Particles: Structural and Kinetic Analyses of Photocatalytic Reaction in Aqueous Alcohol and Amino Acid Solutions. *J. Phys. Chem. B* **1997**, *101*, 3349–3359. [CrossRef]