Effect of copper ions on the formation of hydrogen peroxide from photocatalytic titanium dioxide particles

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Abstract

Reactive radicals such as hydroxyl radical (OH·), hydrogen peroxide (H_2O_2), and superoxide anion ($O_2{}^-$) are the main power driving titanium dioxide (TiO_2) photocatalytic reactions, for example, photokilling of biological cells. Here, the effect of copper ions on the formation of H_2O_2 over photocatalytic TiO_2 was investigated. Under an oxygen-purged solution, formation of H_2O_2 was increased dramatically up to 20 times by the addition of a small amount of copper ions. By using the Fenton reaction, the H_2O_2 formed can be converted into OH·, a highly reactive radical. In contrast, under nitrogen-purged solution, no H_2O_2 was formed even in the presence of an electron acceptor, silver ion (Ag^+). These results clearly show that H_2O_2 was generated from the reduction site of the photoexcited TiO_2 and indicate an effective way to increase the photocatalytic efficiency.
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1. Introduction

In recent years, photocatalytic reactions with TiO_2 have been investigated worldwide for various applications [1–5]. One idea is to use such photochemical reactions to kill biological cells [6–9]. Under light irradiation, we found that biological cells can be killed effectively when TiO_2 particles (300 Å) are incorporated into the cells, or when the biological cells are cultured on the surface of a TiO_2-coated substrate. Using this effect, we suggested that ultra fine TiO_2 particles can be used for the treatment of skin tumors or skin disease, and that TiO_2-coated substrates can be used as antibacterial materials.

The mechanism of cell death by the TiO_2 photochemical reaction involves photogenerated holes and reactive oxygen such as OH·, $O_2{}^-$, and H_2O_2 [6,7]. The formation of these reactive species from the photoexcited TiO_2 is generally considered to occur as follows. Illumination of TiO_2 with a photon energy greater than the band gap (3.23 eV = 384 nm for pure anatase) excites an electron from the valance band to the conduction band, leaving a positively charged hole in the valence band. This positive hole will oxidize water to OH·, and the negative electron will reduce oxygen to $O_2{}^-$. Therefore, the valence band edge and conduction band edge respectively represent the oxidation site and the reduction site of a photocatalytic TiO_2 particle. As the OH· formed is very reactive, and the valence band edge of TiO_2 was reported to be 2.6 V (vs SCE) [10], the reaction occurring at the oxidation site is thought to be very strong and important. In relation, $O_2{}^-$ generated from the reduction site is thought to be less reactive, and not so important in the photocatalysis process [11,12]. On the other hand, the formation of H_2O_2 from a photocatalytic TiO_2 particle was proposed through various processes [13,14]. One view suggests that it is produced at the oxidation site; another theory proposes that it is generated at the reduction site [15,16].

Further, the photocatalytic efficiency is a key issue to overcome in consideration of various applications because TiO_2 is excited by UV light only. In our previous work, we successfully monitored the electron transfer from photoexcited TiO_2 particle to dissolved oxygen (O_2), and then to an

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active center of superoxide dismutase (SOD) [16]. We made positive use of $O_2{}^-$, the primary product from the reduction site, by converting it into H_2O_2 and $OH^{\cdot}$ in the presence of SOD and the Fenton reagent [17]. As a result, the photocatalytic cell-killing effect was increased [18]. However, the weak point in this case is that the photoexcited TiO_2 will oxidize the bioenzyme, resulting in it being unable to sustain such conversions.

In this paper, instead of a biological enzyme, copper ions were used to investigate the formation of H_2O_2. The amount of H_2O_2 produced in the TiO_2 suspension was measured under oxygen-purged and nitrogen-purged conditions both with and without electron acceptors. This was carried out to clarify if H_2O_2 was generated from the reduction site or the oxidation site of TiO_2 particles. We also converted H_2O_2 into the most reactive $OH^{\cdot}$ in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA)–Fe. As copper ion in this study is more stable compared with the previously used SOD enzyme, we believe that this is an effective way to increase the photocatalytic efficiency.

2. Experimental

Formation of H_2O_2 was carried out as in the previous study [17]. At first, 300 mg of TiO_2 particles (p-25; Nippon Aerosil Co., Tokyo, Japan) was dispersed in 3 ml of distilled water. Copper chloride ($CuCl_2$; copper (II)) solution was added into it, making final concentrations of 10, 20, 30, and 40 µM copper (II) solutions, respectively. Fenton reagents were prepared by mixing ferrous sulfate ($FeSO_4$; Tokyo Kasei Co.) and EDTA (Tokyo Kasei Co.) and then were adjusted to the targeted concentration. All above solutions were freshly prepared throughout the experiment. The pH for the final solution was adjusted to 4.5. Pure O_2 (or N_2) gas was bubbled through the TiO_2 suspension for 30 min and sealed by O_2 (or N_2) overflow. It was then irradiated for 5 min by UV light from a 500-W high-pressure Hg lamp (Ushio Co., Tokyo, Japan). During irradiation, a UV pass filter (UVD2, Toshiba Co.) was used to transmit a wavelength of 300–400 nm. After irradiation, the TiO_2 particles were removed by filtration through a 0.22-mm membrane filter, and the H_2O_2 content of the filtered solution was measured. The concentration of H_2O_2 was measured by a fluorescent assay reported by Perschke and Broda [19]. In this method, scopolectin dye was oxidized by H_2O_2 (H_2O_2 is a quencher of scopolectin). The intensity of the fluorescence was decreased in the presence of H_2O_2. When 0.1 ml of scopolectin solution (5×10^{-5} M) was added to various standard concentrations of H_2O_2 (without TiO_2 particles), the intensity of fluorescence at 460 nm from each sample was measured. The relationship between the fluorescence intensity of the scopolectin and the amount of H_2O_2 is shown in Fig. 1. One can see that upon addition of H_2O_2 to the scopolectin solution, I_{arb} was decreased dramatically. This decrease shows a linear drop from 1 to 10 µM H_2O_2. For instance, addition

of 4.7 µM H_2O_2 reduced I_{arb} to almost its half value, and 10 µM H_2O_2 resulted in I_{arb} being decreased to zero. Using a standard curve, an unknown H_2O_2 concentration can be determined by measurement of the fluorescence peak intensity of scopolectin.

3. Results and discussion

We investigated a series of control experiments. They are: (1) UV irradiation of solution without the addition of TiO_2; and (2) addition of copper ions to the solution without UV irradiation. All these experiments showed no effect on scopolectin fluorescence measurement. In the presence of TiO_2 particles, the formation of H_2O_2 was studied with and without UV irradiation. With TiO_2 particles in the dark, I_{arb} was 100 as seen in the inset of Fig. 1 (curve 1a), where various fluorescence spectra of scopolectin solutions are shown under different conditions. With TiO_2 particles plus 5 min UV irradiation, I_{arb} was decreased to 92 as indicated in curve 1b. Further addition of 40 µM copper (II) into the above solution (with exposure to UV for 5 min) reduced I_{arb} to 10 (curve 1c). Using the relationship curve shown in Fig. 1, we found that the amounts of H_2O_2 formed in experiments 1b and 1c were 0.4 and 8.0 µM, respectively. As no H_2O_2 was detected in the dark, we can conclude that the
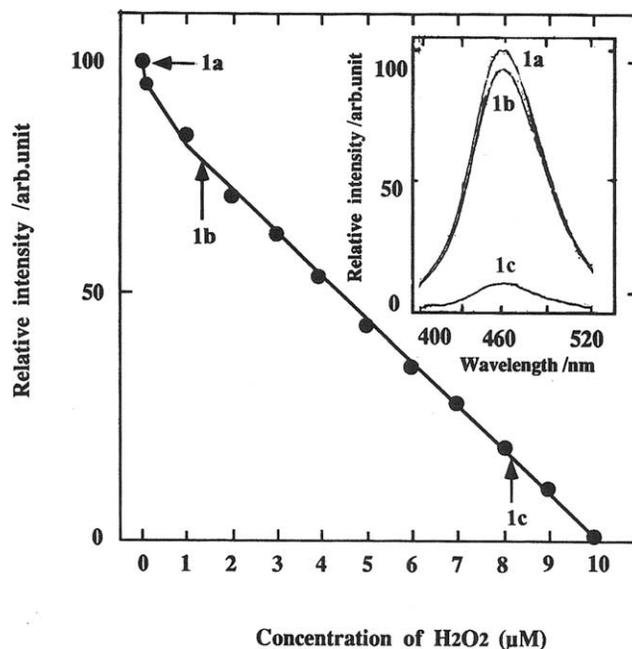

Fig. 1. Fluorescence intensity of scopolectin at 460 nm as a function of H_2O_2 concentration. Curves 1a, 1b, and 1c in the inset represent the fluorescence spectra of scopolectin under different conditions. In this case, three types of solutions were prepared. The first sample (curve 1a) was with TiO_2 in the dark. The second sample (curve 1b) was with TiO_2 after 5 min irradiation. The third sample (curve 1c) was with TiO_2 and 40 µM copper (II) ion added followed by further irradiation for 5 min. All these three samples were used for scopolectin fluorescence measurement as described under Experimental.
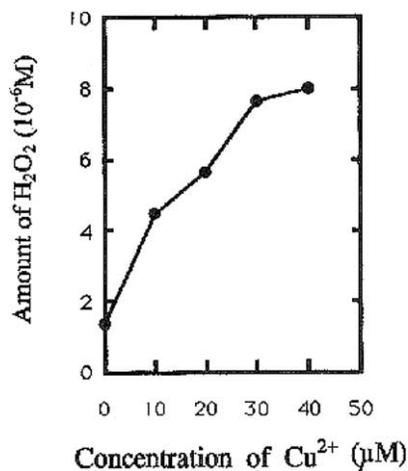
Fig. 2. The effect of copper (II) ion concentration on formation of H_2O_2 produced from TiO_2 particles under 5 min UV irradiation.

H_2O_2 is generated from photocatalytic TiO_2, and its formation was accelerated by the addition of a copper (II) solution. Here, almost 20 times as much H_2O_2 was produced in the presence of a 40 μM copper (II) solution.

The effect of copper (II) concentration on formation of H_2O_2 was investigated. For this purpose, various concentrations of copper (II) solution were added into a TiO_2 suspension, and the previous experiment was repeated. When copper (II) solutions were added at 10, 20, 30, and 40 μM, the concentrations of H_2O_2 formed were 4.8, 5.8, 7.8, and 8.0 μM, respectively. The relationship between copper (II) solution concentration and the amount of H_2O_2 is shown in Fig. 2. The amount of H_2O_2 leveled off when the concentration of copper (II) solution reached the range of 30–40 μM. Considering the amount of H_2O_2 generated at the highest level, it is worth noting that the amount of H_2O_2 induced by copper (II) solution in the present study is twice as high as that achieved by using the bioenzyme catalyst, SOD [17]. The efficiency of H_2O_2 production by SOD was found to be sensitive to the environment. It was deactivated by the photoexcited TiO_2, resulting in a loss of enzyme function. Solution age and the used surrounding temperature also largely affect SOD activity. In contrast, the copper (II) solutions in this case are very stable. The reason for stability is probably due to reduction of oxygen prevailing over the reduction of copper (II) ion under the oxygen atmosphere. Foster et al. described that on illumination of an oxygen-purged solution, Cu(II) ions concentrations were increased by release from Cu–TiO_2 particles. On the other hand, upon purging with nitrogen, Cu(II) ions in the supernatant were deposited onto the surface of TiO_2 [20]. Similarly, we found that copper (II) was only deposited on TiO_2 particles in the presence of radical scavengers under nitrogen-purged solution, but not deposited under oxygen-purged solution (unpublished data). It is reasonable to assume that Cu(II) ions in the present study are not reduced. Instead, the dissolved oxygen is thought to react with the photogenerated electron to form O_2^- (see Fig. 3).
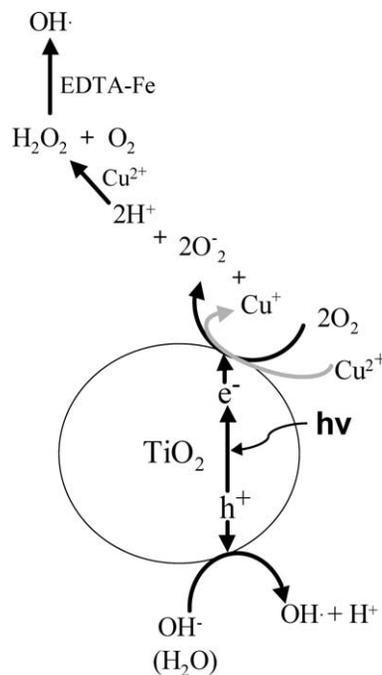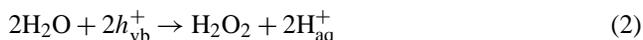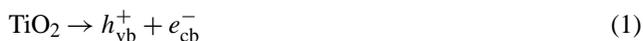

Fig. 3. Schematic illustration of the photocatalytic formation of H_2O_2 and $OH^{\cdot}$ in the presence of copper (II) ion and Fenton reagent.

Formation of H_2O_2 from TiO_2 particles has been proposed by many researchers [11–16]. Two alternative mechanisms are proposed. One process involves oxidation of water by photogenerated holes via reactions (1) and (2). In the other process, dissolved oxygen is reduced by photogenerated electron via reaction (3). Here, h_{vb}^+ and e_{cb}^- are the photogenerated hole in the

$$TiO_2 \rightarrow h_{vb}^+ + e_{cb}^- \tag{1}$$

$$2H_2O + 2h_{vb}^+ \rightarrow H_2O_2 + 2H_{aq}^+ \tag{2}$$

$$O_2 + 2e_{cb}^- + 2H_{aq}^+ \rightarrow H_2O_2 \tag{3}$$

valence band and the electron in the conduction band, respectively. These reactions are expected to occur on the TiO_2 surface. To clarify which process contributes to the H_2O_2 formation in this study, we deaerated TiO_2 suspension by using nitrogen gas and then measured the H_2O_2 amount in the presence of copper (II) solution (silver ions from AgCl were even used as electron acceptor). It is particularly surprising that no H_2O_2 was detected in the deaerated TiO_2 suspension. Also, when the TiO_2 suspension was kept without UV irradiation, no H_2O_2 was detected. These facts indicate that oxygen and UV irradiation are both necessary for the formation of H_2O_2. Therefore, we can say that H_2O_2 was formed from the reduction of dissolved oxygen via reaction (3) and was not produced at oxidation sites through reactions (1) and (2). This conclusion agrees well with our previous result, in which SOD was employed [17].

It is well known that reactive radicals such as O_2^-, H_2O_2, and $OH^{\cdot}$ are the main contributors to TiO_2 photocatalytic reactions. Among them, $OH^{\cdot}$ is the most reactive. On the other hand, EDTA–Fe is a well-known Fenton reagent for
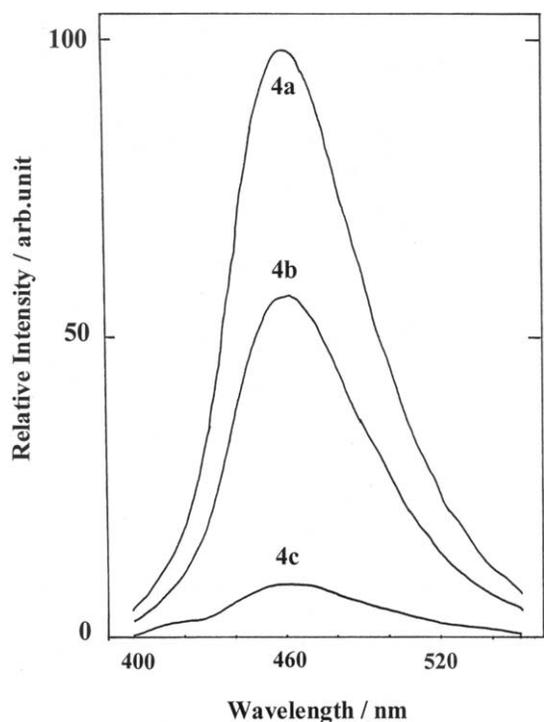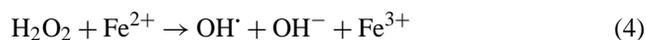
Fig. 4. Fluorescence spectra of scopolectin under different conditions: curve 4a, TiO_2 particle alone; curve 4b, TiO_2 + 40 µM copper (II) ion + 20 µM EDTA–Fe + 5 min irradiation; curve 4c, TiO_2 + 40 µM copper (II) ion + 5 min irradiation.

converting H_2O_2 into OH· via reaction (4) [21], and its effect in the

$$H_2O_2 + Fe^{2+} \rightarrow OH· + OH^- + Fe^{3+} \tag{4}$$

TiO_2/copper (II) ion system was further studied. In Fig. 4, with TiO_2 particles in the dark, no H_2O_2 was formed and I_{arb} was 100. When 40 µM copper (II) solution was added to TiO_2 suspensions under UV irradiation, I_{arb} was decreased to 10 (curve 4c in Fig. 4). However, the intensity of I_{arb} recovered up to 58 upon addition of 20 µM EDTA–Fe (curve 4b in Fig. 4). This suggests that H_2O_2 was used as a source to generate OH· via reaction (4). If more OH· is produced, higher photocatalytic efficiency is expected. In fact, it was found that the rate of cell killing was increased 3-fold by using SOD and the Fenton reagent to convert O_2^- into H_2O_2, and H_2O_2 into OH·, respectively [18]. To increase the TiO_2 photocatalytic efficiency, some researchers have added H_2O_2 into TiO_2 suspension [22–24]. For example, photocatalytic oxidation of phenol was reported to be significantly accelerated by addition of H_2O_2 together with transition-metal ions such as Fe^{3+} and Cu^{2+} [22,23]. They reported that Cu^{2+} did not cause the intensive short-circuiting problem which usually happens in the photocatalytic oxidation process when adding transition ions alone [24]. Walling et al. described that H_2O_2 was decomposed into hydroxyl radicals by UV irradiation [25]. This conversion was also accelerated in the presence of ferric ions [26]. Similarly, Fujihira et al. reported that the quantum yield of photocatalytic oxidation of aromatic compounds by TiO_2 was increased about

16 times in the presence of copper (II) ion [21]. However, if H_2O_2 alone were added, it was chemisorbed onto TiO_2 at low pH, to give a surface peroxo complex [27]. This surface-adsorbed peroxo complex significantly inhibited photooxidation of methyl orange [28]. Thus, one new finding from the present study is to combine the H_2O_2-enhanced effect on copper (II) ion with the Fenton reaction to achieve a higher photocatalytic efficiency.

In the past, rare metals (platinum, silver, palladium) and copper have generally been deposited onto the surface of TiO_2 particle in order to increase the photocatalytic efficiency [29,30]. In this case, the deposited metal acts as an electron acceptor, resulting in efficient charge separation, to intensify the hole and OH· effect. In the present study, as copper ions will not be reduced under oxygen-purged conditions, we can say that the role of the copper ions is different from that of deposited copper.

At this stage, it is clear that H_2O_2 production is accelerated by copper (II) ions, but the mechanism by which the copper (II) ion catalyzes H_2O_2 production is still unclear. We assume that it may proceed as with SOD through the following reactions:

$$O_2^- + Cu(II) \rightarrow O_2 + Cu(I) \tag{5}$$

$$O_2^- + 2H^+ + Cu(I) \rightarrow H_2O_2 + Cu(II) \tag{6}$$
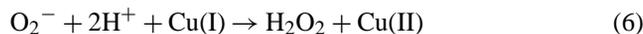
Indeed, we found that pH changes during reaction and confirmed that reactions (5) and (6) are possible as the pathway. In another experiment, when oxygen was totally removed, we found that the TiO_2 photocatalytic oxidation of H_2S gas was almost stopped (unpublished data). This fact indicates that oxygen is a key component in the photochemical reaction. In the past, Heller and co-workers studied the role of oxygen in the photooxidation and reported that the rate of photooxidation of organic compounds on the surface of a catalyst is limited by the rate of electron transfer to the oxygen [2]. Here, we show that various types of reactive oxygen are produced from photocatalytic TiO_2 particles under an oxygen atmosphere, especially in the presence of copper (II) ion and EDTA–Fe together. Less reactive species can convert into more reactive ones, which in turn oxidize organic substances. Like this, controlling the conversion of radicals generated from the reduction site can alter the rate of the photocatalytic reaction. Our experimental evidence suggests that chemical reactions occurring at the reduction site of TiO_2 particles are equally important as those occurring at the oxidation site.

4. Conclusions

The results in this study are summarized in Fig. 3. In the presence of copper (II) ions, O_2^- generated from reduction sites on TiO_2 particles was effectively converted into H_2O_2. The H_2O_2 formed was also converted into a highly reactive OH· radical in the presence of Fenton reagent. Our experiment also suggests the possibility that Cu(I) can also be

formed by reduction by the conduction band electrons of irradiated TiO_2 in competition with reduction of molecular oxygen to give the superoxide radical anion. Compared with biological enzyme, the copper (II) ion used in this study is more stable. We believe that such a system can be potentially applied to various applications where TiO_2 photocatalysts are currently being employed for destruction of organic pollutants in water.

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