

# Bifunctionality of Rh<sup>3+</sup> Modifier on TiO<sub>2</sub> and Working Mechanism of Rh<sup>3+</sup>/TiO<sub>2</sub> Photocatalyst under Irradiation of Visible Light

著者	Kitano Sho, Murakami Naoya, Ohno Teruhisa, Mitani Yasufumi, Nosaka Yoshio, Asakura Hiroyuki, Teramura Kentaro, Tanaka Tsunehiro, Tada Hiroaki, Hashimoto Keiji, Kominami Hiroshi
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# Bifunctionality of Rh<sup>3+</sup> modifier on TiO<sub>2</sub> and working mechanism of Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst under irradiation of visible light

*Sho Kitano,<sup>†</sup> Naoya Murakami,<sup>‡</sup> Teruhisa Ohno,<sup>‡</sup> Yasufumi Mitani,<sup>§</sup> Yoshio Nosaka,<sup>§</sup> Hiroyuki*

*Asakura,<sup>¶</sup> Kentaro Teramura,<sup>¶</sup> Tsunehiro Tanaka,<sup>¶</sup> Hiroaki Tada,<sup>#</sup> Keiji Hashimoto,<sup>#</sup> Hiroshi*

*Kominami<sup>#,\*</sup>*

<sup>†</sup>Interdisciplinary Graduate School of Science and Engineering, Kinki University, 3-4-1

Kowakae, Higashiosaka, Osaka 577-8502, Japan.

<sup>‡</sup>Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, 1-1

Sensuicho, Tobata, Kitakyushu 804-8550, Japan.

<sup>§</sup>Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka 940-2188, Japan.

<sup>¶</sup>Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan.

<sup>#</sup>Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashiosaka, Osaka 577-8502, Japan.

**ABSTRACT:** A rhodium(III) ion ( $\text{Rh}^{3+}$ )-modified  $\text{TiO}_2$  ( $\text{Rh}^{3+}/\text{TiO}_2$ ) photocatalyst, prepared by a simple adsorption method and exhibiting high levels of photocatalytic activity in degradation of organic compounds, was investigated by using X-ray absorption fine structure (XAFS) measurements, (photo)electrochemical measurements, double-beam photoacoustic (DB-PA) spectroscopic measurements and photoluminescence measurements. Based on the results, the features of the  $\text{Rh}^{3+}$  modifier and the working mechanism of the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst are discussed. XAFS measurements revealed that the  $\text{Rh}^{3+}$  species were highly dispersed and almost atomically isolated on  $\text{TiO}_2$ . The (photo)electrochemical measurements, DB-PA spectroscopic measurements and photoluminescence showed a unique bifunction of the  $\text{Rh}^{3+}$  modifier as a promoter for  $\text{O}_2$  reductions and an electron injector to the conduction band of  $\text{TiO}_2$  for response to visible light. The reasons for the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst exhibiting higher levels of photocatalytic activity than those of  $\text{TiO}_2$  photocatalysts modified with other metal ions are also discussed on the basis of obtained results.

## 1. Introduction

Titanium(IV) oxide ( $\text{TiO}_2$ ) is an efficient photocatalyst that has strong oxidation abilities and widely used for many practical applications.<sup>1-3</sup> However,  $\text{TiO}_2$  only works under irradiation of UV light due to its wide band gap, 3.2 eV (anatase), and many technologies have been developed

to make TiO<sub>2</sub> respond to visible light for efficient utilization of solar or indoor light.<sup>4-22</sup> Surface modification of TiO<sub>2</sub> with transition metals is one of the important methods to visualize TiO<sub>2</sub>-based photocatalysts.<sup>10-22</sup> In this method, various transition metals are not doped in lattices but are just fixed on the surface of TiO<sub>2</sub>, and charge transfers occur between the metals and TiO<sub>2</sub> under irradiation of visible light. These photocatalysts have flexibility and variation because there are many candidates of transition metals as modifiers, and properties of TiO<sub>2</sub> supports can be controlled to maximize photocatalytic activities in objective reactions.

Kisch *et al.* reported TiO<sub>2</sub> photocatalysts modified with inorganic sensitizers including platinum(IV) and rhodium(III) chlorides.<sup>10, 11</sup> These metal chloride-modified photocatalysts were prepared by the impregnation method using TiO<sub>2</sub> powders and metal sources followed by calcination for fixation. In platinum chloride-modified photocatalysts, a platinum chloride absorbs visible light and splits a Pt<sup>III</sup> intermediate and a surface-bound chlorine atom due to homolytic Pt<sup>IV</sup>-Cl bond cleavage. A Pt<sup>III</sup> intermediate injects an electron into the conduction band of TiO<sub>2</sub> and a chlorine atom oxidizes substrates, and they return to initial states. In rhodium chloride-modified photocatalysts, a rhodium-to-titanium charge transfer transition (from a rhodium chloride to the conduction band of TiO<sub>2</sub>) occurs under irradiation of visible light, and an electron injected in the conduction band and a Rh<sup>IV</sup> center which oxidizes substrates are generated. The electrons in the conduction band are accepted by O<sub>2</sub>.

Recently, TiO<sub>2</sub> photocatalysts modified with molecular metal oxide species introduced by using the chemisorption-calcination cycle (CCC) technique have been reported by one of authors of this paper.<sup>12-14</sup> In these photocatalysts, electronic excitation occurs from the surface d sub band to the conduction band of TiO<sub>2</sub> under irradiation of visible light, and the holes generated in the d sub band oxidized substrates, while the surface iron oxide species promote O<sub>2</sub> reduction.

Ohno and Murakami, also authors of this paper, have reported TiO<sub>2</sub> photocatalysts modified with metal ions.<sup>15</sup> The photocatalysts were easily prepared by stirring a suspension of TiO<sub>2</sub> in a metal chloride solution followed by filtration and drying (*no heat treatment*). In these photocatalysts, metal ion species were probably fixed as metal oxides or hydroxide clusters. The metal ion species inject electrons into the conduction band of TiO<sub>2</sub> under irradiation of visible light and become an oxidative state that oxidizes substrates. The metal ion species also works as electron acceptors from the conduction band of TiO<sub>2</sub> like a cocatalyst.

On the other hand, a different working mechanism has been proposed by Irie *et al.* despite using a similar photocatalyst system.<sup>16-18</sup> They suggested that the interfacial charge transfer (IFCT) from the valence band of TiO<sub>2</sub> to redox potentials of the metal ion species<sup>16-18</sup> occurs under irradiation of visible light and that the holes generated in the valence band oxidize the substrates. The metal ion species that have accepted electrons reduce O<sub>2</sub> molecules through multi-electron reduction and then return to the initial states.

These *modified* photocatalysts have been mainly used for mineralization of harmful organic compounds; however, it is expected that they can be applied to various other reactions due to their properties as described above. For application of these *modified* photocatalysts to various reactions, it is important to analyze and clarify their features in detail. Although the working mechanisms and features of these photocatalysts and the states of modifiers have been partially investigated using some measurements in the reports, there have been few reports on their detailed characterization.

Recently, we have developed a new photocatalyst responding to visible light, rhodium(III) ion-modified TiO<sub>2</sub> (Rh<sup>3+</sup>/TiO<sub>2</sub>). Modification of TiO<sub>2</sub> with Rh<sup>3+</sup> was very simple; it was achieved only by adsorption from an Rh<sup>3+</sup> solution and subsequent drying at a moderate temperature (*no*

*calcination*), resulting in small energy consumption in the preparation process. We have reported that this photocatalyst exhibited higher levels of activities than those of TiO<sub>2</sub> photocatalysts modified with other metal ions in mineralization of volatile organic compounds (VOC) under irradiation of visible light.<sup>20-22</sup> Results obtained in those studies indicate that the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst works by a unique mechanism and that Rh species fixed on the surface of TiO<sub>2</sub> work as electron injectors or sensitizers for response to visible light. Comparable studies using anatase- and rutile-type TiO<sub>2</sub> have suggested that Rh species also act as promoters for O<sub>2</sub> reduction by electrons injected in the conduction band of TiO<sub>2</sub> similar to photocatalysts reported by Ohno *et al.*<sup>15</sup> However, the working mechanism and the reason why the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst exhibits excellent photocatalytic activities are still unclear. In this study, we investigated functions of Rh species fixed on TiO<sub>2</sub> by using various methods such as X-ray absorption fine structure (XAFS) measurements, (photo)electrochemical measurements, double-beam photoacoustic (DB-PA) spectroscopic measurements and photoluminescence measurements. Based on the results, we discuss bifunctionality of Rh species fixed on TiO<sub>2</sub> and the working mechanism of the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst under irradiation of visible light.

## 2. Experimental

### 2.1. Sample preparation

All of the chemicals were used as received without further purification. Semiconductor oxide supports, TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>, were synthesized by the HyCOM (Hydrothermal Crystallization in Organic Media) method reported previously to obtain samples having a large specific surface area.<sup>23-24</sup> Commercial samples from Kanto Nanotek were used for SnO<sub>2</sub>. HyCOM-TiO<sub>2</sub>, HyCOM-Ta<sub>2</sub>O<sub>5</sub> and SnO<sub>2</sub> powders were calcined at 550, 800 and 500°C,

respectively, in a box furnace for 1 h. The samples were modified with  $\text{Rh}^{3+}$  by the equilibrium method.<sup>20-22</sup> The samples were added to an aqueous solution of rhodium(III) chloride, the charged amount of which corresponded to 1.0 wt% of  $\text{Rh}^{3+}$ , and stirred and heated in a water bath at *ca.* 90°C. The suspension was filtered and the filtrate was washed repeatedly with distilled water and then the filtrate was dried *in vacuo* for 1 h. The amount of  $\text{Rh}^{3+}$  fixed on  $\text{TiO}_2$  was determined by analysis of  $\text{Rh}^{3+}$  in the filtrate using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500).

The  $\text{Rh}^{3+}$  species in the prepared samples were modified only on the surface of oxide supports since thermal treatment was not carried out after modification with  $\text{Rh}^{3+}$ , which is different from element-doped photocatalysts calcined at high temperature. Thus, the  $\text{Rh}^{3+}$  species did not exist in the bulk of supports like dopants, often working as recombination centers. In addition, most of the chloride, which is generally thought to be a cause of deactivation, on the prepared samples was eliminated by elaborate washing.

## 2.2. Characterization

Powder X-ray diffraction (XRD) was measured using  $\text{CuK}\alpha$  radiation by a Rigaku MultiFlex equipped with a carbon monochromator. Specific surface area ( $S_{\text{BET}}$ ) of the samples was measured using the Brunauer-Emmett-Teller (BET) single-point method on the basis of nitrogen ( $\text{N}_2$ ) uptake measured at -196°C using a Shimadzu Flowsorb 2300. Diffuse reflectance spectra of the samples were measured using a Shimadzu UV-2400 UV-Vis spectrometer equipped with a diffuse reflectance measurement unit (ISR-2000) and recorded after Kubelka–Munk analysis. Rh K-edge XAFS spectra of the as-prepared  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst and reference samples (Rh foil and  $\text{Rh}_2\text{O}_3$ ) were recorded at the BL01B1 beamline at the SPring-8 (Japan Synchrotron

Radiation Research Institute, Hyogo, Japan) in the transmission mode for Rh foil and Rh<sub>2</sub>O<sub>3</sub> and fluorescence mode for Rh<sup>3+</sup>/TiO<sub>2</sub> samples at ambient temperature. An Si (311) two-crystal monochromator was used to obtain a monochromatic X-ray beam. The photon energy was calibrated at the inflection point of the absorption edge of an X-ray absorption near edge structure (XANES) spectrum of Rh foil. Higher harmonics were removed by slight detuning of the monochromator. Data reduction was carried out with Athena and Artemis included in the Ifeffit package.

The features of Rh<sup>3+</sup> were analyzed by electrical measurement. A slurry of HyCOM-TiO<sub>2</sub> particles (HyCOM-TiO<sub>2</sub> 0.05 g/ethylene glycol 0.01 ml) was coated on conductive glass (F-doped SnO<sub>2</sub>, 10 Ω/cm<sup>2</sup>) by a squeegee method, and the electrode was heated at 823 K for 1 h, and then the HyCOM-TiO<sub>2</sub> electrode was modified with Rh<sup>3+</sup> by the same method as that described above. Photocurrent and current-potential curves of the electrodes were measured in a 0.1 M-NaClO<sub>4</sub> electrolyte solution in a regular three-electrode electrochemical cell on a

galvanostat/potentiostat (HZ-5000, Hokuto Denko) under atmosphere. A Xe lamp with a Y-43 cut filter (85 mW cm<sup>-2</sup>, 400 - 600 nm) was used as the source of visible light. Glassy carbon and an Ag/AgCl electrode (TOA-DKK) were used as the counter electrode and reference electrode, respectively.

The behaviors of electrons on samples in gas phase were analyzed by DB-PA spectroscopic measurements. A gas-exchangeable photoacoustic cell equipped with two valves for gas flow was used, and a sample was placed in the cell. The atmosphere was controlled by a flow of artificial air or N<sub>2</sub> containing ethanol vapor (air + EtOH, N<sub>2</sub> + EtOH), and the measurements were conducted after shutting off the valves, i.e., in a closed system at room temperature. An LED emitting light at ca. 625 nm (Luxeon LXHL-ND98) was used as a probe light, and the



output intensity was modulated by a digital function generator (NF DF1905) at 80 Hz. In addition to the modulated light, a UV-LED (Nichia NCCU033, 365 nm, 1.6 mW cm<sup>-1</sup>) and a blue LED (Luxeon LXHL-NB98, 470 nm, 3.6 mW cm<sup>-1</sup>) were also used as simultaneous continuous irradiation for photoexcitation of samples. The PA signal acquired by a condenser microphone buried in the cell was amplified and monitored by a digital lock-in amplifier (NF LI5640).

Detailed setups of DB-PA spectroscopic measurements have been reported.<sup>25</sup>

Active oxygen species formed in reactions using an Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst were measured by chemiluminescence (CL) photometry.<sup>26-29</sup> The formation of O<sub>2</sub><sup>•-</sup> was observed by using a luminol CL probe method. A quartz cell (1 cm-1 cm) containing a photocatalyst (15 mg) suspension in 3.5 mL of 0.01 M NaOH solution was placed in a dark box and irradiated with a 14 mW He-Cd laser (KIMMON, IK5652R-G) at the wavelength of 442 nm. Immediately after the laser irradiation, 50 μL of 7 mM luminol solution was injected via a microsyringe into the irradiated suspension. The CL intensity was measured with a Peltier-cooled photon counter head (Hamamatsu, H7421), and number of photons counted was integrated over 100 s. Other details of the apparatus and the CL reaction have been reported previously.<sup>27</sup> The experimental procedure for the selective detection of H<sub>2</sub>O<sub>2</sub> is basically the same as the O<sub>2</sub><sup>•-</sup> measurement

except for the injection solution and the timing. The suspension was mounted in the dark box in the same place as that for the O<sub>2</sub><sup>•-</sup> measurement. After irradiation of the photocatalysts, the suspension was kept in the dark for 30 min for elimination of O<sub>2</sub><sup>•-</sup>, and then 50 μL of 7 mM luminol solution (0.01 M NaOH) was added. The suspension containing luminol was kept again for 10 min in the dark. Then 50 μL of hemoglobin (Hb) solution was injected via a

microsyringe into the suspension and the time profile of CL intensity was measured repeatedly. To convert the observed CL intensities to the absolute concentrations of O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub>, the

apparatus factor was calculated from the experiment in which all luminal molecules are consumed for the reaction with an excess amount of  $\text{H}_2\text{O}_2$ .

### 2.3. Evaluation of photocatalytic activity under irradiation of visible light

A sample (30 mg) was suspended in a small amount of distilled water and then the powder was spread on a glass filter (GF-75, 26 mm in diameter, Advantec) with a Buchner funnel under suction. The glass filter together with the sample was dried *in vacuo* for 1 h. The glass filter together with the sample and a glass vessel containing an aqueous solution of acetone (1 vol%) were placed in a glass reactor. The gas phase in the system was replaced with artificial air (oxygen ( $\text{O}_2$ ) (20%)-nitrogen ( $\text{N}_2$ ) gas mixture), and acetone was gradually evaporated and then the vapor was saturated in the reactor. After adsorption of acetone had reached an equilibrium, the photocatalyst was irradiated by visible light or UV light, of which the intensities on the surface of the glass filter were  $95 \text{ mW cm}^{-2}$  (400-600 nm) and  $120 \text{ mW cm}^{-2}$  (300-450 nm), respectively. The amounts of acetone and  $\text{CO}_2$  were determined by a gas chromatograph (Agilent Technologies, A3000 micro GC).

## 3. Results and discussion

### 3.1. XAFS analysis for state of Rh species on the surface of $\text{TiO}_2$

In previous studies,<sup>20-22</sup> we investigated activities of  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalysts and the effect(s) of physical properties of  $\text{TiO}_2$  samples on the activities. However, states of Rh species fixed on  $\text{TiO}_2$  were hardly investigated. Here, the states and the surrounding condition of Rh species were analyzed by XAFS measurements.

Figure 1A shows Rh K-edge XANES spectra of Rh foil, rhodium(III) oxide ( $\text{Rh}_2\text{O}_3$ ) and  $\text{Rh}^{3+}/\text{TiO}_2$  samples. Figure 1B shows an enlargement of XANES spectra in Figure 1A. The spectrum of the  $\text{Rh}^{3+}/\text{TiO}_2$  sample was similar to that of  $\text{Rh}_2\text{O}_3$  but different from that of Rh foil. The absorption edge energy of Rh species of  $\text{Rh}^{3+}/\text{TiO}_2$  (23 215.5 eV) is comparable to that of  $\text{Rh}_2\text{O}_3$  (23 215.2 eV), indicating that the oxidation state of Rh species of  $\text{Rh}^{3+}/\text{TiO}_2$  is trivalent. Figure 2 shows Fourier transforms (FT) of  $k^3$ -weighted Rh K-edge EXAFS spectra of  $\text{Rh}_2\text{O}_3$  and  $\text{Rh}^{3+}/\text{TiO}_2$  samples. The Fourier-transformed spectrum of  $\text{Rh}_2\text{O}_3$  shows three peaks at around 1.60, 2.64, and 3.34 Å, which are attributed to the scatterings by Rh-O and a couple of Rh-Rh shells, respectively. However, the Fourier-transformed spectrum of  $\text{Rh}^{3+}/\text{TiO}_2$  exhibits only a single peak at 1.60 Å, which is due to the Rh-O shell. The clear difference in spectral features strongly suggests that the  $\text{Rh}^{3+}$  species are highly dispersed and almost atomically isolated on  $\text{TiO}_2$ .

This is clearly different from Cu and Fe species reported by Irie and coworkers, which were grafted as amorphous oxyhydroxide clusters on  $\text{TiO}_2$ .<sup>17, 18</sup> The isolated  $\text{Rh}^{3+}$  was probably modified as a complex-like form coordinated by the surface hydroxyl group of  $\text{TiO}_2$  and  $\text{H}_2\text{O}$  since we confirmed that chlorides were almost completely eliminated by washing with distilled water in the preparation.

### 3.2. Electrochemical measurements under irradiation of visible light and in the dark

Electrochemical measurements were used to investigate the behavior of electrons in  $\text{Rh}^{3+}/\text{TiO}_2$  under irradiation of visible light and in the dark. Based on the results obtained, the role(s) of  $\text{Rh}^{3+}$  will be discussed. Figure 3 shows time courses of photocurrent measurements of bare  $\text{TiO}_2$  and  $\text{Rh}^{3+}/\text{TiO}_2$  electrodes under irradiation of visible light. A photocurrent was hardly

observed in the bare TiO<sub>2</sub> electrode, indicating that band-gap excitation of TiO<sub>2</sub> was negligible under the present irradiation conditions. On the other hand, a large anodic photocurrent was observed when the Rh<sup>3+</sup>/TiO<sub>2</sub> electrode was used. The observed anodic current means that electrons transferred from the working electrode to the counter electrode through the circuit.

These results for the bare TiO<sub>2</sub> and Rh<sup>3+</sup>/TiO<sub>2</sub> electrodes suggest that electrons transferred from Rh<sup>3+</sup> to the conduction band of TiO<sub>2</sub> in the latter electrode under irradiation of visible light. The photocurrent decreased in the initial stage. However, thereafter a stable constant photocurrent was observed, indicating that Rh<sup>3+</sup> fixed on TiO<sub>2</sub> works as a stable electron injector.

Figure 4 shows current (*I*, milliamps)-potential (*E*, plots vs. NHE) curves of the bare TiO<sub>2</sub> and Rh<sup>3+</sup>/TiO<sub>2</sub> electrodes in the dark in the presence of air. A current was hardly observed in the

absence of O<sub>2</sub> in both electrodes. In the case of the bare TiO<sub>2</sub> electrode in the presence of air, the current did not flow at the potential range between 0 and 0.4 V. Below 0 V, a small current due to O<sub>2</sub> reduction was observed. This current corresponded to one-electron reduction of O<sub>2</sub> (O<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> = HO<sub>2</sub>, E<sup>0</sup> = -0.046 V).<sup>30</sup> On the other hand, a larger current of O<sub>2</sub> reduction was observed when the Rh<sup>3+</sup>/TiO<sub>2</sub> electrode was used. These results indicate that Rh<sup>3+</sup> fixed on the surface of TiO<sub>2</sub> greatly promoted electron transfer from TiO<sub>2</sub> to O<sub>2</sub> molecules. It should be noted that the potential at which the current started to flow shifted toward the positive region (ca. 0.15 V) in the case of the Rh<sup>3+</sup>/TiO<sub>2</sub> electrode. This potential is in good agreement with the redox potentials of Rh<sup>3+</sup> (Rh<sup>3+</sup> + e<sup>-</sup> = Rh<sup>2+</sup>, E<sup>0</sup> = 0.158 V; Rh<sup>3+</sup> + 2e<sup>-</sup> = Rh<sup>+</sup>, E<sup>0</sup> = 0.158 V).<sup>30</sup> At this potential, multi-electron reductions of O<sub>2</sub> (two-electron reduction: O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> = H<sub>2</sub>O<sub>2</sub>, E<sup>0</sup> = 0.68 V; or four-electron reduction: O<sub>2</sub> + 4H<sup>+</sup> + 4e<sup>-</sup> = 2H<sub>2</sub>O, E<sup>0</sup> = 1.23 V)<sup>30</sup> are possible because the redox potential of Rh<sup>3+</sup> is more positive than that of one-electron reduction of O<sub>2</sub> and more negative than that of multi-electron reductions of O<sub>2</sub>. Therefore, it can be concluded from the

electrochemical behaviors of the bare  $\text{TiO}_2$  and  $\text{Rh}^{3+}/\text{TiO}_2$  electrodes in the dark that the  $\text{Rh}^{3+}$  species accepted electrons from  $\text{TiO}_2$  at 0.158 V, resulting in the formation of reduced Rh species ( $\text{Rh}^{2+}$  or  $\text{Rh}^+$ ) and that the reduced Rh species transferred electrons to  $\text{O}_2$  molecules through their multi-electron reductions. Active oxygen species formed by reduction of  $\text{O}_2$  molecules in the  $\text{Rh}^{3+}/\text{TiO}_2$  suspension system were also investigated and will be discussed later (section 3.5).

### 3.3. DB-PA spectroscopic measurement under irradiation of UV or visible light

DB-PA spectroscopic measurement enables detection of electrons in the conduction band of  $\text{TiO}_2$  by detection of trivalent titanium ( $\text{Ti}^{3+}$ ) species reduced.<sup>15, 25</sup> Thus, behaviors of electrons in samples during reactions can be directly analyzed by the DB-PA spectroscopic measurement. Electrochemical measurements enable accurate analysis of redox potentials and electrical properties of samples. However, electrochemical measurements indicate reactions occurring between molecules and the electrode in the *solid-liquid* interface. Ince  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalysts were used for degradation of VOC, the photocatalysts were set in air containing VOC.<sup>20-22</sup> Therefore, the behaviors of Rh species and/or electrons in the *solid-gas* interface should also be evaluated. In this sense, the DB-PA spectroscopic measurement is important to understand the behaviors of Rh species and/or electrons in  $\text{Rh}^{3+}/\text{TiO}_2$  in the solid-gas photocatalytic reaction. Figure 5 shows time courses of PA signals of bare  $\text{TiO}_2$  and  $\text{Rh}^{3+}/\text{TiO}_2$  samples under irradiation of visible light from a blue LED in the presence of  $\text{N}_2$  and ethanol (deaerated condition). Under this condition, holes in the valence band of  $\text{TiO}_2$  are consumed by ethanol, while electrons in the conduction band accumulate because of the absence of appropriate electron acceptors such as  $\text{O}_2$  molecules. The PA signal of the bare  $\text{TiO}_2$  sample did not

increase, indicating that no band gap excitation in TiO<sub>2</sub> occurred under irradiation of visible light. Meanwhile, the PA signal of the Rh<sup>3+</sup>/TiO<sub>2</sub> sample gradually increased. This result shows that electron transfer in the Rh<sup>3+</sup>/TiO<sub>2</sub> sample and accumulation of electrons in TiO<sub>2</sub> (formation of Ti<sup>3+</sup>) occurred under visible light irradiation in the absence of O<sub>2</sub>. Formation of Ti<sup>3+</sup> was helpful for determining the path of photoexcitation, i.e., formation of Ti<sup>3+</sup> means that electrons transferred to the conduction band of TiO<sub>2</sub> by irradiation of visible light. Taking into account the band-gap of TiO<sub>2</sub>, energy of visible light irradiated and the results for photoelectrochemical response of the Rh<sup>3+</sup>/TiO<sub>2</sub> electrode, we can conclude that the response of Rh<sup>3+</sup>/TiO<sub>2</sub> to visible light originated from the charge transfer from Rh<sup>3+</sup> to the conduction band of TiO<sub>2</sub>.

Figure 6 shows time courses of PA signals of bare TiO<sub>2</sub> and Rh<sup>3+</sup>/TiO<sub>2</sub> samples under irradiation of UV light in the presence of artificial air (N<sub>2</sub>:O<sub>2</sub> = 80:20) and ethanol. In this condition, electrons generated in the conduction band by band-gap excitation under irradiation of UV light were consumed by reduction of O<sub>2</sub> molecules. Thus, O<sub>2</sub> reduction ability of samples at the gas-solid interface was evaluated using this PA method. The signal does not increase if the excited electrons immediately transfer to O<sub>2</sub> molecules. The PA signal of bare TiO<sub>2</sub> steeply increased and was gradually saturated, indicating that accumulation of electrons occurred due to relatively slow consumption of electrons, i.e., reduction of O<sub>2</sub>, and then accumulation and consumption of electrons tended to reach an equilibrium with prolongation of irradiation. On the other hand, the PA signal of Rh<sup>3+</sup>/TiO<sub>2</sub> was almost unchanged before and after irradiation of UV light. This result indicates that electrons excited to the conduction band by UV irradiation immediately transferred to O<sub>2</sub>; i.e., the reduction of O<sub>2</sub> was drastically promoted by Rh<sup>3+</sup> as was observed in electrochemical measurement (Figure 4). It has been reported that PA signals of various TiO<sub>2</sub> samples modified with other metal ions also decreased compared to that of bare

TiO<sub>2</sub>, under the almost same condition of this report.<sup>15</sup> It should be noted that a small signal was observed in the case of TiO<sub>2</sub> samples modified with other metal ions, whereas a signal of Rh<sup>3+</sup>/TiO<sub>2</sub> was hardly observed, indicating that Rh<sup>3+</sup> has a higher level of O<sub>2</sub> reduction ability than that of other metal ions. Therefore, from the results of electrochemical and DB-PA spectroscopic measurements, we can conclude that Rh<sup>3+</sup> fixed on Ti effectively works as a promoter for the reduction of O<sub>2</sub>.

### 3.4. Investigation of the mechanism of charge transfer from Rh<sup>3+</sup> to the conduction band of supports

Results of photoelectrochemical analysis and PAS revealed that electrons were injected from Rh species to the conduction band of TiO<sub>2</sub> under irradiation of visible light. However, the results are not sufficient to clarify the excitation mechanism since two excitation routes have been revealed in several studies: 1) indirect charge transfer in which electrons in Rh<sup>3+</sup> are excited and then move to the conduction band of TiO<sub>2</sub> like a sensitizer system<sup>10</sup> as shown in Figure 7(A) and 2) direct charge transfer from Rh<sup>3+</sup> to the conduction band of TiO<sub>2</sub> as shown in Figure 7(B). For investigating which charge transfer occurs, some semiconductor oxides having various energy levels of the conduction band were modified with Rh<sup>3+</sup> and the photocatalytic activity of the samples was evaluated using decomposition of VOC in gas phase under irradiation of visible or UV light. Some semiconductor metal oxides were synthesized by HyCOM methods<sup>23, 24</sup> giving nanocrystalline metal oxides with a large specific surface area that is suitable for modification with a large amount of Rh<sup>3+</sup> and thus enabling clear observation of the effect of Rh<sup>3+</sup> modification.

Table 1 shows the physical properties of various metal oxides. The metal oxides have band gaps larger than that of  $\text{TiO}_2$ , indicating that they do not respond to visible light. Figure 8(A) shows diffuse reflection spectra of bare metal oxides and emission spectra of visible light and UV light. All samples showed photoabsorption corresponding to their band-gap excitations. The  $\text{SnO}_2$  sample also showed a shoulder in the visible light region due to oxygen vacancies, which did not contribute to the photocatalytic activity under irradiation of visible light. Figure 8(B) shows diffuse reflection spectra of  $\text{Rh}^{3+}$ -modified samples and emission spectra of visible and UV light. All modified samples exhibited additional photoabsorption in a longer wavelength region. The photoabsorption in the range around 450 nm originated from  $d-d$  transition of Rh,  $^1A_{1g} \rightarrow ^2T_{2g}$ <sup>11, 33</sup>. The photoabsorption in the range from visible to UV light regions probably originated from the charge transfer from  $\text{Rh}^{3+}$  to the conduction band of semiconductors, which depends on the semiconductor oxide.

Figure 9 shows rates of  $\text{CO}_2$  formation in decomposition of gaseous acetone, a VOC, over the  $\text{Rh}^{3+}$ -modified samples under irradiation of visible light from the blue LED. No  $\text{CO}_2$  was formed over any of the bare samples due to insufficient energy of the blue light for band-gap excitation of the semiconductors. The  $\text{Rh}^{3+}$ -modified  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{SnO}_2$  samples exhibited photocatalytic activity for degradation of acetone, whereas the  $\text{Rh}^{3+}$ -modified  $\text{Ta}_2\text{O}_5$  sample did not. These results indicate that the charge transfer from  $\text{Rh}^{3+}$  to the conduction band of the semiconductors by visible light occurs only when the energy levels of the conduction bands of the semiconductors are located close to or below that of the conduction band of  $\text{TiO}_2$ . Figure 10 shows the rates of  $\text{CO}_2$  formation for decomposition of gaseous acetone over bare and  $\text{Rh}^{3+}$ -modified  $\text{Ta}_2\text{O}_5$  samples under irradiation of UV light. The bare  $\text{Ta}_2\text{O}_5$  sample showed almost no photocatalytic activity, indicating that the energy required for the band-gap excitation of



Ta<sub>2</sub>O<sub>5</sub> was slightly larger than that of UV light irradiated. On the other hand, acetone was mineralized over Rh<sup>3+</sup>-modified Ta<sub>2</sub>O<sub>5</sub> under UV irradiation, indicating that another route for charge separation was created by modification of Ta<sub>2</sub>O<sub>5</sub> with Rh<sup>3+</sup>. If the route created by modification of Ta<sub>2</sub>O<sub>5</sub> with Rh<sup>3+</sup> is the indirect charge transfer route, the Rh<sup>3+</sup>-modified Ta<sub>2</sub>O<sub>5</sub> sample would not exhibit photocatalytic activity under irradiation of UV light because the energy required for excitation of the Rh<sup>3+</sup> species and indirect charge transfer do not depend on the type of semiconductors in experiments on visible light excitation. If the direct route from Rh<sup>3+</sup> to the conduction band of Ta<sub>2</sub>O<sub>5</sub> is created, whether the charge transfer occurs or not should depend on the energy of light irradiated to Rh<sup>3+</sup>-modified Ta<sub>2</sub>O<sub>5</sub>. Experimental results for photocatalytic activity of Rh<sup>3+</sup>-modified Ta<sub>2</sub>O<sub>5</sub> indicate that the excitation of electrons occurred via direct charge transfer from Rh<sup>3+</sup> to the conduction band of Ta<sub>2</sub>O<sub>5</sub>. In addition, it was supported by the fact that the absorption due to the charge transfer depends on the semiconductors as shown in Figure 8(B). Therefore, it can be concluded that charge separation in Rh<sup>3+</sup>-modified semiconductor photocatalysts under irradiation of light occurred directly from Rh<sup>3+</sup> to the conduction band of semiconductors.

The photocatalytic activities of these samples cannot be easily compared since the physical properties of supports, the amount of Rh<sup>3+</sup> modified and further factors of the samples were not optimized. The effects of supports on the photocatalytic activity of Rh<sup>3+</sup>-modified photocatalysts will be reported separately.

### 3.5. Investigation of active oxygen under irradiation of visible light

The bifunction of Rh<sup>3+</sup> was discussed in previous sections. However, it is important to clarify not only the behaviors of electrons in the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst but also active oxygen species

formed by  $\text{Rh}^{3+}/\text{TiO}_2$  because the latter information would reveal the whole working mechanism including interactions between the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst and oxygen molecules. Thus, CL photometry was carried out for investigation of active oxygen species produced by photocatalysis of  $\text{Rh}^{3+}/\text{TiO}_2$  under irradiation of visible light.

Figure 11 shows time courses of  $\text{O}_2^{\bullet -}$  and  $\text{H}_2\text{O}_2$  formed by  $\text{Rh}^{3+}/\text{TiO}_2$  under irradiation of visible light. The  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst produced  $\text{H}_2\text{O}_2$  under irradiation of visible light, indicating that  $\text{Rh}^{3+}$  on  $\text{TiO}_2$  obviously worked as a co-catalyst for formation of  $\text{H}_2\text{O}_2$  through two-electron reduction of  $\text{O}_2$ . Moreover, the amount of  $\text{H}_2\text{O}_2$  formed by  $\text{Rh}^{3+}/\text{TiO}_2$  was much larger than that of  $\text{H}_2\text{O}_2$  formed by a  $\text{Cu}^{2+}$ -grafted  $\text{TiO}_2$  photocatalyst (less than 1 nM) reported previously under the same condition of this report.<sup>29</sup> This result indicates that  $\text{Rh}^{3+}$  possesses higher activity than that of  $\text{Cu}^{2+}$  in multi-electron reduction of  $\text{O}_2$ .

The  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst also formed a very large amount of  $\text{O}_2^{\bullet -}$  and the concentration reached a steady value around 200 nM. This amount was larger than that formed by other photocatalysts responding to visible light, *i.e.*, doped  $\text{TiO}_2$  photocatalysts (nitrogen-doped  $\text{TiO}_2$ : 180 nM, sulfur-doped  $\text{TiO}_2$ : 70 nM).<sup>28</sup> In the  $\text{Rh}^{3+}/\text{TiO}_2$  sample, one-electron reduction of  $\text{O}_2$  occurred by direct migration of electrons from the conduction band of  $\text{TiO}_2$  to  $\text{O}_2$  molecules since anatase-type  $\text{TiO}_2$  was used as a support for  $\text{Rh}^{3+}$ . The potential of the conduction band of anatase-type  $\text{TiO}_2$ , *i.e.*, -0.2 V (vs NHE),<sup>31, 32</sup> is higher than the redox potential of one-electron reduction of  $\text{O}_2$ . In doped  $\text{TiO}_2$  photocatalysts, nitrogen or sulfur are substituted to lattice atoms in the bulk of  $\text{TiO}_2$ , resulting in insertion of energy levels of the dopant in the forbidden band of  $\text{TiO}_2$  and response to visible light due to excitation from the inserted energy level to the conduction band. However, the dopants often work as recombination sites, which decrease the photocatalytic performance. On the other hand,  $\text{Rh}^{3+}$  probably does not work as recombination

site since  $\text{Rh}^{3+}$  was not doped in bulk but just fixed on the surface of  $\text{TiO}_2$  in the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst. In this sense, modification with  $\text{Rh}^{3+}$  would be more advantageous than doping ions to prepare visible-light-responding photocatalysts using  $\text{TiO}_2$ .

The results of CL photometry clarified that  $\text{Rh}^{3+}/\text{TiO}_2$  produced both  $\text{H}_2\text{O}_2$  and  $\text{O}_2^{\bullet-}$  through two- and one-electron reduction of  $\text{O}_2$ , respectively. The concentrations of  $\text{H}_2\text{O}_2$  and  $\text{O}_2^{\bullet-}$  were much larger than those of  $\text{H}_2\text{O}_2$  and  $\text{O}_2^{\bullet-}$  formed by other photocatalysts responding to visible light,  $\text{Cu}^{2+}$ -grafted  $\text{TiO}_2$  and doped photocatalysts. It is interesting that the redox potentials of  $\text{Rh}^{3+}$  to  $\text{Rh}^{2+}$  and  $\text{Rh}^+$  are the same ( $E^0 = 0.158 \text{ V}$ ) as discussed in section 3.2, indicating that  $\text{Rh}^{2+}$  is unstable. Therefore, it is generally expected that two-electron reduction of  $\text{Rh}^{3+}$  to  $\text{Rh}^+$  easily occurs. This means that two-electron reduction of an  $\text{O}_2$  molecule is possible at an  $\text{Rh}^+$  species ( $\text{O}_2 + \text{Rh}^+ + 2\text{H}^+ = \text{H}_2\text{O}_2 + \text{Rh}^{3+}$ ). In the case of the Cu co-catalyst system, double amounts of the reduced Cu species are required to achieve two-electron reduction of an  $\text{O}_2$  molecule ( $\text{O}_2 + 2\text{Cu}^+ + 2\text{H}^+ = \text{H}_2\text{O}_2 + 2\text{Cu}^{2+}$ ) because the  $\text{Cu}^+ - \text{Cu}^{2+}$  redox system only provides one electron. Therefore, a binuclear structure of Cu species would be required for two-electron reduction of  $\text{O}_2$  molecules by the Cu co-catalyst system. In fact, Irie *et al.* reported that oxyhydroxide clusters were formed on the  $\text{TiO}_2$  surface in a  $\text{Cu}/\text{TiO}_2$  photocatalyst.<sup>17</sup> On the other hand, no binuclear structure would be necessary for the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst because two-electron reduction of one  $\text{O}_2$  molecule is possible at one  $\text{Rh}^+$  species. As shown in Figure 2, Rh species were fixed on the surface of  $\text{TiO}_2$  in an isolated dispersion, indicating that there is almost no binuclear structure of Rh species on  $\text{TiO}_2$  in the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst. This structural result is in good agreement with both electrochemical properties of Rh species and reduction behavior of  $\text{O}_2$  molecules over the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst.

### 3.6. Working mechanism of Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst and features of bifunctional Rh<sup>3+</sup>

Results obtained by XAFS measurements, electrochemical measurements, DB-PA spectroscopic measurements, CL photometry and photocatalytic reactions suggest the working mechanism of the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst and the roles of Rh<sup>3+</sup> shown in Figure 12. Under irradiation of visible light, Rh<sup>3+</sup> directly injects electrons into the conduction band of TiO<sub>2</sub>. The formed Rh species having a higher oxidation state oxidize substrates and return to the initial and stable oxidation state. Electrons injected to the conduction band move and some of them directly transfer to O<sub>2</sub> molecules through one-electron reduction and then O<sub>2</sub><sup>•-</sup> molecules are formed, and the others are accepted by other Rh<sup>3+</sup> and then reduced Rh species i.e., Rh<sup>+</sup>, are formed. The reduced Rh species rapidly reduce O<sub>2</sub> molecules through multi-electron reduction and return to the trivalent state, and H<sub>2</sub>O<sub>2</sub> (two-electron reduction) is mainly formed. Therefore, Rh<sup>3+</sup> can work as a bifunctional modifier: as an electron donor under irradiation of visible light and as a promoter for multi-electron reduction of O<sub>2</sub>. All of the Rh<sup>3+</sup> species fixed on TiO<sub>2</sub> may not act as both electron injectors and promoters for O<sub>2</sub> reduction. It is known that TiO<sub>2</sub> has particular crystal faces on which oxidation or reduction preferentially proceeds.<sup>34, 35</sup> The role of Rh<sup>3+</sup> might depend on crystal faces on which the Rh species were fixed and Rh<sup>3+</sup> might work as either a promoter of O<sub>2</sub> reduction or an electron injector. However, it is clear from results obtained by various methods that Rh species possess both functions.

In mineralization of organic substrates over the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst under irradiation of visible light, it is thought that oxidative decomposition of substrates is mainly performed by photoexcited Rh species having a higher oxidative state rather than by active oxygen species. From the results of XAFS measurements, the Rh<sup>3+</sup> was fixed in an almost atomically isolated state, whereas Cu<sup>2+</sup> and Fe<sup>3+</sup> on TiO<sub>2</sub> were loaded in cluster forms as reported previously.<sup>16-18</sup>

Thus, the Rh<sup>3+</sup>/TiO photocatalyst has many active sites for both electron injection and oxidation of organic compounds (acetone in this study). It is interesting that the highest level of activity was obtained when the surface density of Rh<sup>3+</sup> was 0.65 nm<sup>-2</sup> (Figure S1). These many active sites are one of the reasons for high levels of activity of the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst. In fact, Cu<sup>2+</sup> and Fe<sup>3+</sup>-grafted TiO<sub>2</sub> samples prepared as previously reported<sup>18</sup> exhibited the lower levels of activity (0.33 and 0.21 μmol h<sup>-1</sup>) than that of Rh<sup>3+</sup>/TiO<sub>2</sub> (2.2 μmol h<sup>-1</sup>) in this evaluation as described in section 3.4. In addition, Rh<sup>3+</sup> species work as single sites for two-electron reduction of O<sub>2</sub> because of the redox between Rh<sup>3+</sup> and Rh<sup>+</sup>. For Cu<sup>2+</sup> and Fe<sup>3+</sup>, two or more ions must contribute to the two-electron reduction as described in section 3.5. The optimum surface densities of Cu<sup>2+</sup> and Fe<sup>3+</sup> were reported to be 2.6 and 1.5 nm<sup>-2</sup>, respectively.<sup>18</sup> The fact that the optimum density of Rh<sup>3+</sup> (0.65 nm<sup>-2</sup>) is smaller than those of Cu<sup>2+</sup> and Fe<sup>3+</sup> also suggests that a single site structure was formed in the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst. The single site structure of the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst is attributed to its effective H<sub>2</sub>O<sub>2</sub> formation compared with Cu<sup>2+</sup>-grafted TiO<sub>2</sub>.<sup>29</sup> Therefore, the excellent properties of Rh<sup>3+</sup> both as a promoter for O<sub>2</sub> reduction and an electron injector under irradiation of visible light resulted in higher levels of photocatalytic activity of the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst than those of other photocatalyst responding to visible light.

Taken together, the results revealed that the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst has unique features that other *modified* photocatalysts do not have. It is expected that the photocatalyst can be applied not only for oxidative decomposition of VOC but also for various photocatalyst systems. A study of reaction systems in which the Rh<sup>3+</sup>/TiO<sub>2</sub> photocatalyst exhibits good photocatalytic activities is in progress.

#### 4. Conclusions

The working mechanism of the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst and features of the  $\text{Rh}^{3+}$  modifier were investigated by various methods. The XAFS measurements revealed that the Rh species have a trivalent state and are highly dispersed with an almost atomically isolated state on  $\text{TiO}_2$ .

(Photo)electrochemical measurements, DB-PA spectroscopic measurements and photoluminescence measurements showed that  $\text{Rh}^{3+}$  works as a bifunctional modifier, i.e., a electron injector for response to visible light and the promoter for multi-electron reduction of  $\text{O}_2$ . The  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst has many active sites due to the isolated dispersion of  $\text{Rh}^{3+}$ , which is different from  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  on  $\text{TiO}_2$  photocatalysts consisting of cluster forms. In addition,  $\text{Rh}^{3+}$  species are capable of working as single sites for two-electron reduction of  $\text{O}_2$  because of the redox between  $\text{Rh}^{3+}$  and  $\text{Rh}^+$  in contrast to the one-electron redox of  $\text{Cu}^{2+}-\text{Cu}^+$  and  $\text{Fe}^{3+}-\text{Fe}^{2+}$ . Therefore, these excellent and unique properties of  $\text{Rh}^{3+}$  as a bifunctional modifier resulted in higher levels of photocatalytic activities of the  $\text{Rh}^{3+}/\text{TiO}_2$  photocatalyst than those of other photocatalysts responding to visible light.

#### ASSOCIATED CONTENT

**Supporting Information.** Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### AUTHOR INFORMATION

##### Corresponding Author

\*E-mail address: [hiro@apch.kindai.ac.jp](mailto:hiro@apch.kindai.ac.jp) (H. Kominami)

**Present Addresses**

†Hiroyuki Asakura, Synchrotron Radiation Research Center, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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**Figure captions**

**Figure 1.** A) Rh K-edge XANES spectra of Rh foil,  $\text{Rh}_2\text{O}_3$  and  $\text{Rh}^{3+}/\text{TiO}_2$  samples. B) Enlargement of part A.

**Figure 2.** Fourier transforms (FT) of  $k^3$ -weighted Rh-K edge EXAFS spectra of  $\text{Rh}_2\text{O}_3$  and  $\text{Rh}^{3+}/\text{TiO}_2$  samples.

**Figure 3.** Time courses of photocurrent using a)  $\text{Rh}^{3+}/\text{TiO}_2$  and b) bare  $\text{TiO}_2$  electrodes under irradiation of visible light.

**Figure 4.** Current-potential curves of a)  $\text{Rh}^{3+}/\text{TiO}_2$  and b) bare  $\text{TiO}_2$  electrodes under dark in the presence of air.

**Figure 5.** Time courses of PA signals of a)  $\text{Rh}^{3+}/\text{TiO}_2$  and b) bare  $\text{TiO}_2$  samples under irradiation of visible light in the presence of N and ethanol. 2

**Figure 6.** Time courses of PA signals of a)  $\text{Rh}^{3+}/\text{TiO}_2$  and b) bare  $\text{TiO}_2$  samples under irradiation of UV light in the presence of air and ethanol.

**Figure 7.** Assumed schemes of electron transfers from  $\text{Rh}^{3+}$  to the conduction band of  $\text{TiO}_2$  in  $\text{Rh}^{3+}/\text{TiO}_2$  under irradiation of visible light: (A) indirect charge transfer and (B) direct charge transfer.

**Figure 8.** Diffuse reflection spectra of (A) bare and (B)  $\text{Rh}^{3+}$ -modified semiconductor oxide samples and emission spectra of visible and UV light.

**Figure 9.** Rate of CO formation for decomposition of acetone in gas phase under irradiation of visible light using Rh<sup>3+</sup>-modified semiconductor samples.

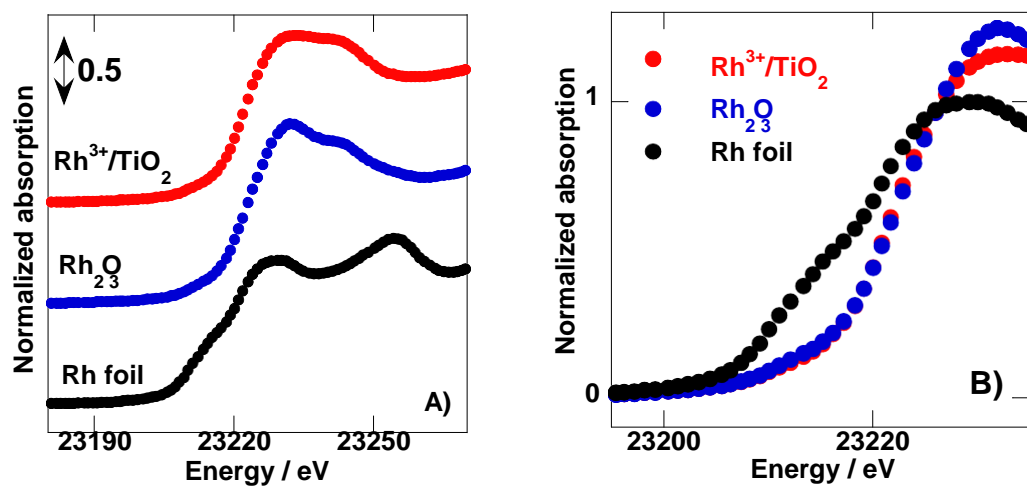
**Figure 10.** Rate of CO<sub>2</sub> formation for decomposition of acetone in gas phase under irradiation of UV light using bare and Rh<sup>3+</sup>-modified Ta<sub>2</sub>O<sub>5</sub> samples.

**Figure 11.** Time courses of O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub> formed by Rh<sup>3+</sup>/TiO<sub>2</sub> under irradiation of visible light.

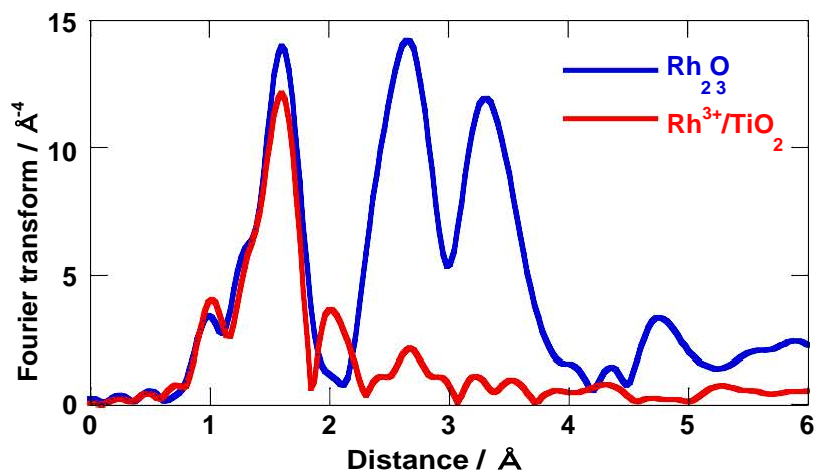
**Figure 12.** Scheme of the working mechanism of the Rh/TiO<sub>2</sub> photocatalyst.

Table 1 Physical properties of various semiconductor samples.

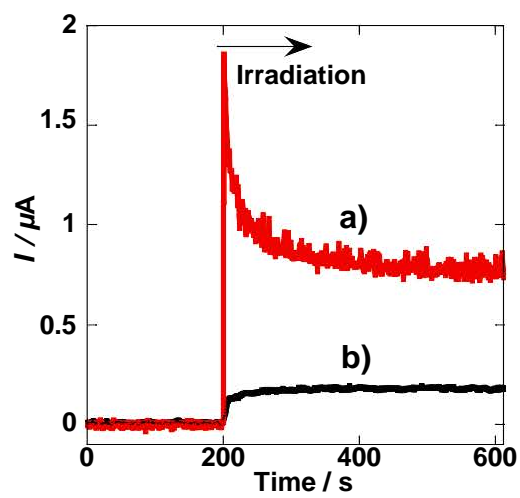
Semiconductor	Conduction band potential / V vs. NHE	Band gap /eV	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>
Ta <sub>2</sub> O <sub>5</sub>	-1.0	4.0	50
TiO <sub>2</sub>	-0.2	3.2	81
Nb <sub>2</sub> O <sub>5</sub>	0.0	3.4	250
SnO <sub>2</sub>	0.5	3.5	30



**Figure 1.** A) Rh-K edge EXAFS spectra of Rh<sub>2</sub>O<sub>3</sub> and Rh<sup>3+</sup>/TiO<sub>2</sub> samples.  
B) Enlargement of part A.

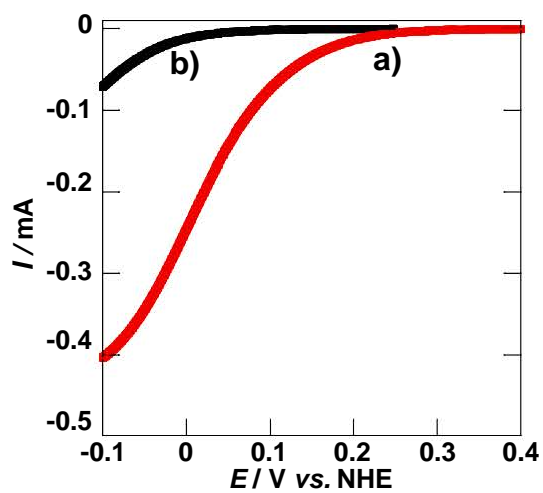


**Figure 2.** Fourier transforms (FT) of  $k^3$ -weighted Rh-K edge EXAFS spectra of  $\text{Rh}_2\text{O}_3$  and  $\text{Rh}^{3+}/\text{TiO}_2$  samples.

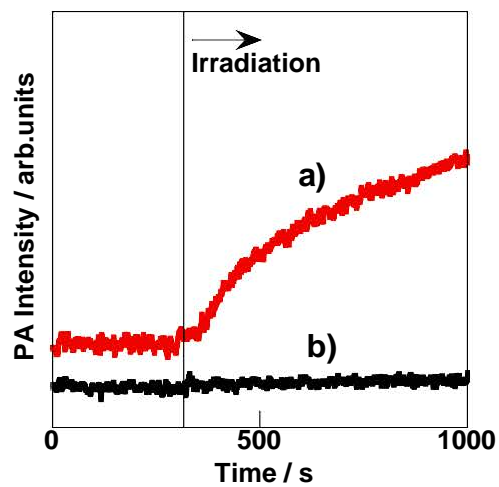


**Figure 3.** Time courses of photocurrent using a) Rh<sup>3+</sup>/TiO<sub>2</sub> and b) bare TiO<sub>2</sub> electrodes under irradiation of visible light.

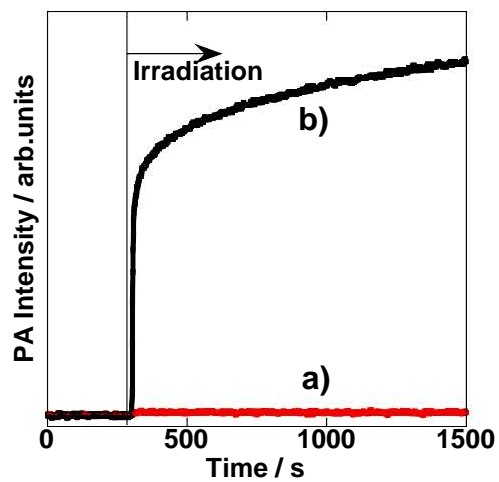




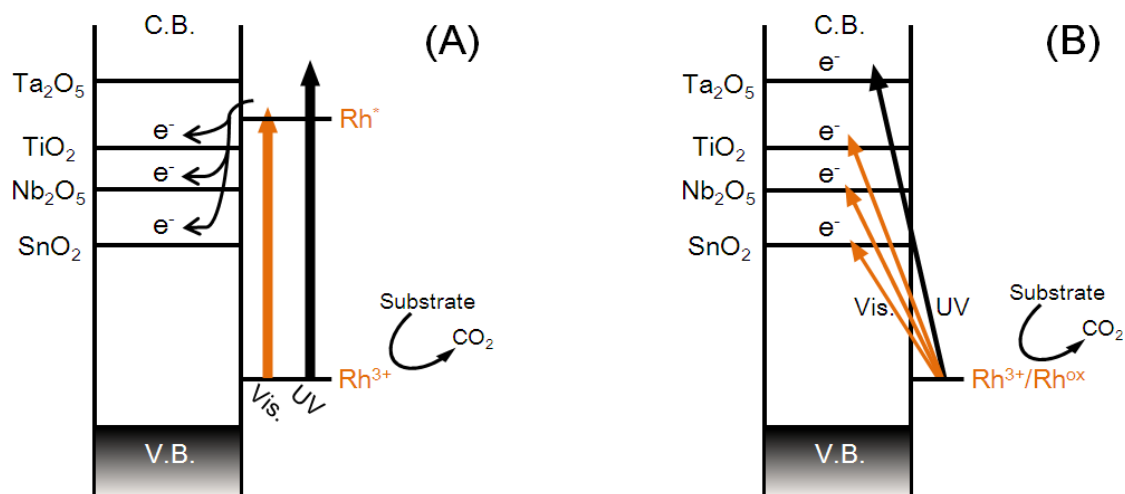
**Figure 4.** Current-potential curves of a)  $\text{Rh}^{3+}/\text{TiO}_2$  and b) bare  $\text{TiO}_2$  electrodes under dark in the presence of air.



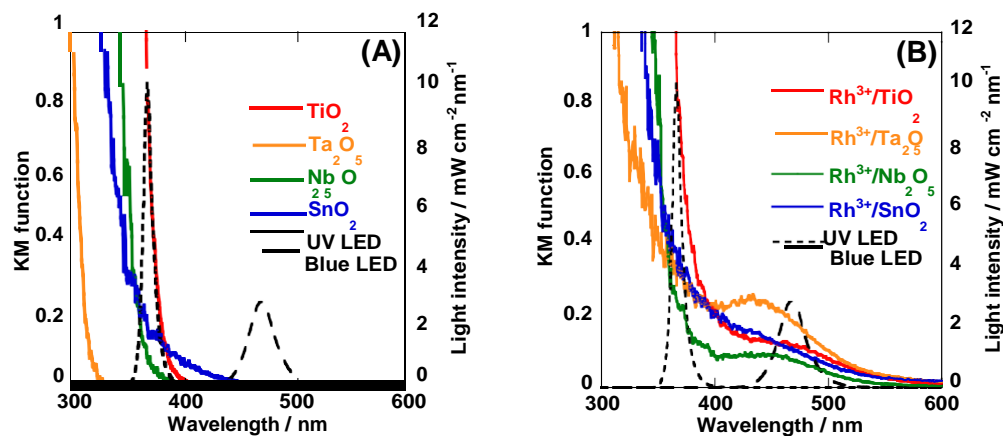
**Figure 5.** Time courses of PA signals of a)  $\text{Rh}^{3+}/\text{TiO}_2$  and b) bare  $\text{TiO}_2$  samples under irradiation of visible light in the presence of  $\text{N}_2$  and ethanol.



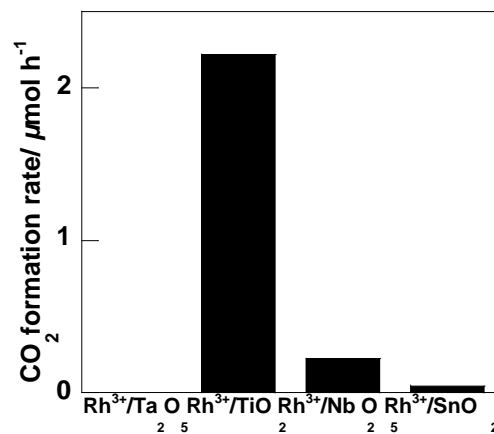
**Figure 6.** Time courses of PA signals of a) Rh<sup>3+</sup>/TiO<sub>2</sub> and b) bare TiO<sub>2</sub> samples under irradiation of UV light in the presence of air and ethanol.



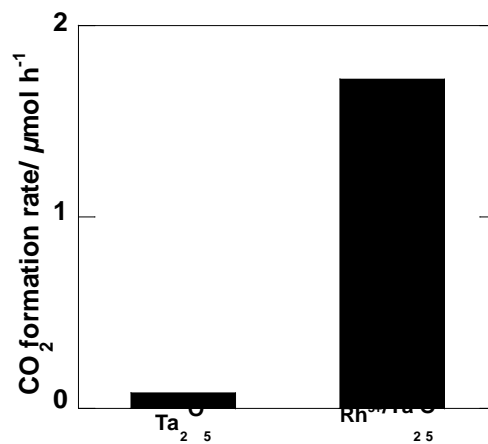
**Figure 7.** Assumed schemes of electron transfers from Rh<sup>3+</sup> to the conduction band of TiO<sub>2</sub> in Rh<sup>3+</sup>/TiO<sub>2</sub> under irradiation of visible light: (A) indirect charge transfer and (B) direct charge transfer.



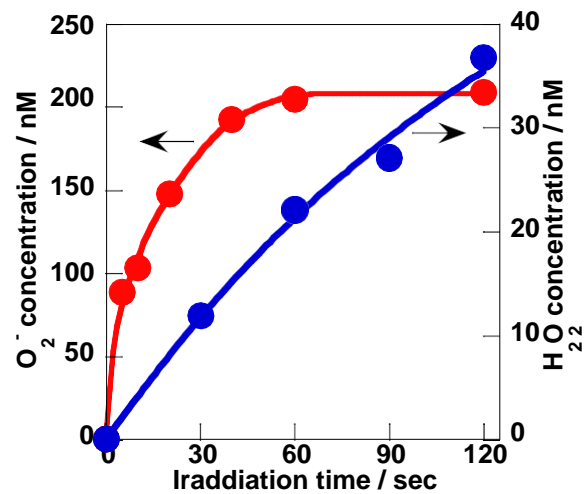
**Figure 8.** Diffuse reflection spectra of (A) bare and (B) Rh<sup>3+</sup>-modified semiconductor oxide samples and emission spectra of visible and UV light.



**Figure 9.** Rate of CO<sub>2</sub> formation for decomposition of acetone in gas phase under irradiation of visible light using Rh<sup>3+</sup>-modified semiconductor samples.

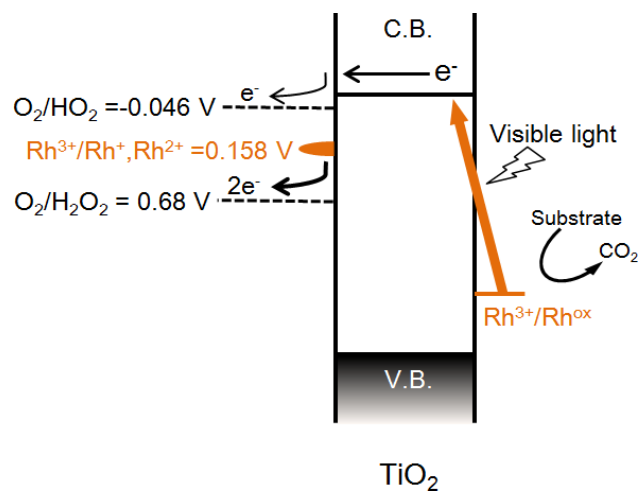


**Figure 10.** Rate of CO<sub>2</sub> formation for decomposition of acetone in gas phase under irradiation of UV light using bare and Rh<sup>3+</sup>-modified Ta<sub>2</sub>O<sub>5</sub> samples.



**Figure 11.** Time courses of  $O_2^{\cdot -}$  and  $H_2O_2$  formed by  $Rh^{3+}/TiO_2$  under irradiation of visible light.





**Figure 12.** Scheme of the working mechanism of the Rh/TiO<sub>2</sub> photocatalyst.

