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## PAPER

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# Preparation of $\text{RhO}_x/\text{TiO}_2$ with Pt cocatalyst effective for photocatalytic alcohol dehydrogenation under irradiation of visible light

Atsuhiko Tanaka, \* Masaaki Fukuda, Takumi Nagai, Hiroyuki Asakura and Hiroshi Kominami \*

Photocatalytic alcohol dehydrogenation is a promising technique for the simultaneous production of hydrogen ( $\text{H}_2$ ) and carbonyl compounds. In this study, titanium(IV) oxide ( $\text{TiO}_2$ ) photocatalysts co-loaded with rhodium oxide ( $\text{RhO}_x$ ) and platinum (Pt) particles were successfully prepared via a multi-step process involving the equilibrium adsorption of Rh ions, post-calcination, and Pt colloid impregnation. In the resulting system,  $\text{RhO}_x$  acts as a visible-light sensitizer, while Pt serves as the hydrogen evolution co-catalyst. A series of  $\text{RhO}_x/\text{TiO}_2$ -Pt samples were synthesized by systematically varying the calcination temperature of the  $\text{RhO}_x/\text{TiO}_2$  precursor prior to Pt loading. These materials were then evaluated for photocatalytic alcohol dehydrogenation under visible light irradiation. The effects of calcination temperature on the electronic states and light absorption characteristics of the Rh species were investigated, along with their influence on photocatalytic activity. The  $\text{RhO}_x/\text{TiO}_2$ -Pt photocatalysts exhibited efficient dehydrogenation of various alcohols. In particular, benzyl alcohol was selectively converted to benzaldehyde and  $\text{H}_2$  in a stoichiometric ratio, with no over-oxidation observed. This work demonstrates a novel strategy for coupling oxidative organic synthesis with hydrogen production under visible light, offering new insights into photocatalyst design for sustainable energy and chemical synthesis.

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## 1. Introduction

Extensive research has been devoted to the development of  $\text{TiO}_2$ -based photocatalysts that respond to visible light. This sustained interest is driven by several key factors, among which the following three stand out:

1.  $\text{TiO}_2$  exhibits exceptional and unrivaled photocatalytic properties;
2. Titanium is an abundant and safe element, making it attractive from both environmental and resource-availability perspectives;
3. There is a strong demand to harness visible light, in addition to ultraviolet (UV) light, for practical photocatalytic applications.

Therefore, narrowing the band gap of  $\text{TiO}_2$  or sensitizing it to visible light is a critical challenge. Various approaches have been explored, such as creating oxygen vacancies, elemental doping (both cationic and anionic), and forming heterostructures.<sup>1</sup> Although these methods have successfully improved visible-light absorption, they sometimes introduce charge recombination centers or exhibit thermal instability.

In this context, surface modification has emerged as a simple and effective strategy for enabling wide-bandgap  $\text{TiO}_2$  to absorb visible light. A variety of surface modifiers have been explored, including transition metals in different chemical forms, halides,<sup>2</sup> hydroxides,<sup>3</sup> metal ions,<sup>4</sup> and oxides,<sup>5</sup> as well as metal complexes<sup>6</sup> and organic compounds.<sup>7</sup> In these modified  $\text{TiO}_2$  systems, the modifying species are not incorporated into the crystal lattice but are instead supported on the surface of the  $\text{TiO}_2$  particles. This surface configuration facilitates efficient charge transfer between the modifiers and  $\text{TiO}_2$  (Fig. 1). Importantly, the surface-bound

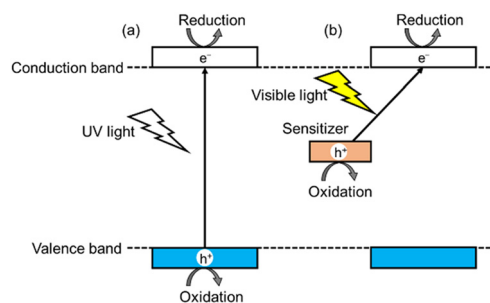


Fig. 1 Proposed energy diagram; (a) band-gap excitation of  $\text{TiO}_2$  and (b) charge transfer from a sensitizer to the CB of  $\text{TiO}_2$ .

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species serve dual roles as visible light absorption centres and oxidation sites.

When  $\text{TiO}_2$ -based photocatalysts are employed for degradation or oxidation reactions under aerated conditions, molecular oxygen ( $\text{O}_2$ ) acts as an effective electron scavenger. The conduction band (CB) potential of  $\text{TiO}_2$  ( $\sim -0.3$  V vs. NHE) is sufficiently negative to drive the reduction of  $\text{O}_2$ , allowing these reactions to proceed without the need for further modification. For instance,  $\text{TiO}_2$  modified with rhodium (Rh) ions has been shown to degrade volatile organic compounds (VOCs) under visible light irradiation.<sup>8</sup> Moreover, selective oxidation of aromatic alcohols has been achieved using  $\text{TiO}_2$  modified with Rh, palladium (Pd), and ruthenium (Ru) ions.<sup>9</sup> The structural evolution of Rh species on  $\text{TiO}_2$  and their influence on photocatalytic performance have also been studied in detail. It was found that calcination-induced changes in  $\text{RhO}_x/\text{TiO}_2$  can significantly affect activity without altering the intrinsic physical properties of  $\text{TiO}_2$ .<sup>10</sup> Notably, atomically isolated  $\text{Rh}^{3+}$  species were identified as the most active form, while aggregation of Rh species led to a marked decline in photocatalytic efficiency.

When  $\text{TiO}_2$ -based photocatalysts (including both unmodified and modified forms) are used for the reduction of a compound under deaerated conditions in the presence of an electron donor, the compound accepts photogenerated electrons either directly or indirectly. In most cases, the incorporation of a co-catalyst is essential to achieve a practical reaction rate and high selectivity for the desired product. A representative example is the hydrogen ( $\text{H}_2$ ) evolution reaction. Given the relatively low overpotential for hydrogen evolution, platinum (Pt) is widely recognized as the most effective co-catalyst. In other systems, the choice of co-catalyst significantly influences selectivity. For instance, in the selective reduction of nitrates to ammonia using an aqueous suspension of a  $\text{TiO}_2$  photocatalyst, copper (Cu) co-catalysts demonstrated superior selectivity.<sup>11</sup> Similarly, silver (Ag) co-catalysts exhibited high activity for the deoxygenation of epoxides in alcoholic suspensions of  $\text{TiO}_2$  photocatalysts.<sup>12</sup> When a modified  $\text{TiO}_2$  photocatalyst is used in conjunction with a co-catalyst, both the visible-light sensitizer (modifier) and the co-catalyst must be introduced onto the  $\text{TiO}_2$  surface. To ensure efficient photocatalytic performance, it is critical to prevent interference between these two components. Therefore, specialized preparation methods are required to preserve and optimize the individual functions of the modifier and the co-catalyst.

Many researchers have reported  $\text{H}_2$  production from various compounds using  $\text{TiO}_2$  photocatalysts under UV irradiation.<sup>13</sup> This approach represents a promising and environmentally friendly technology for generating clean energy from renewable resources. However, UV light accounts for only about 5% of the total solar spectrum, whereas visible light contributes approximately 50%. Consequently, significant research has focused on developing visible-light-responsive photocatalysts for  $\text{H}_2$  production.<sup>14</sup>

Photocatalytic alcohol dehydrogenation has emerged as a particularly attractive route for  $\text{H}_2$  generation.<sup>15</sup> One advantage is its favourable thermodynamics compared to water splitting. For instance, the standard Gibbs free energy change ( $\Delta_r G^0$ ) for ethanol dehydrogenation ( $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{CHO}(\text{l}) + \text{H}_2(\text{g})$ ) is  $47 \text{ kJ mol}^{-1}$ , substantially lower than that for water splitting ( $\Delta_r G^0 = 237 \text{ kJ mol}^{-1}$ ). Additionally, alcohol dehydrogenation produces a valuable carbonyl compound as an oxidation product without requiring any additives. In contrast, achieving selective oxidation to carbonyl compounds using conventional oxidants such as oxygen or permanganate is often challenging. In this study, we applied  $\text{RhO}_x/\text{TiO}_2$  photocatalysts for  $\text{H}_2$  evolution *via* alcohol dehydrogenation under visible light irradiation. To meet the dual requirements of visible-light absorption and efficient hydrogen evolution, a new preparation method was employed. Specifically, Pt colloids were loaded onto  $\text{RhO}_x/\text{TiO}_2$  to introduce small Pt co-catalyst particles. As anticipated, the resulting  $\text{RhO}_x/\text{TiO}_2$ -Pt samples exhibited significantly higher reaction rates compared to co-catalyst-free  $\text{RhO}_x/\text{TiO}_2$  under visible light irradiation. Here, we report the characterization of photocatalysts prepared under various conditions and evaluate their catalytic performance in the dehydrogenation of alcohols under visible light irradiation.

## 2. Experimental section

### 2.1 Synthesis of $\text{TiO}_2$

Nanocrystalline  $\text{TiO}_2$  powder was synthesized *via* hydrothermal crystallization in organic media (HyCOM) at  $300^\circ\text{C}$ .<sup>16</sup> Titanium(IV) butoxide and toluene were used as the titanium precursor and solvent, respectively. The resulting product was calcined at various temperatures for 1 h in a box furnace. Calcination improved the crystallinity of the HyCOM- $\text{TiO}_2$  samples while maintaining a high specific surface area up to  $89 \text{ m}^2 \text{ g}^{-1}$  even after treatment at  $500^\circ\text{C}$ . The  $\text{TiO}_2$  sample calcined at  $500^\circ\text{C}$  was used in most of the subsequent experiments as the support material for Rh species. To investigate the effect of  $\text{TiO}_2$  properties, the HyCOM- $\text{TiO}_2$  sample was calcined at different temperatures. The corresponding pre-calcination temperature ( $T_1$ ) is indicated in parentheses following  $\text{TiO}_2$ ; for example,  $\text{TiO}_2(700)$  refers to the sample calcined at  $700^\circ\text{C}$ .

### 2.2 Preparation of $\text{RhO}_x/\text{TiO}_2$

The  $\text{TiO}_2$  sample was modified with  $\text{Rh}^{3+}$  ions using an equilibrium adsorption method. Pre-calcined  $\text{TiO}_2$  powder was added to an aqueous solution of rhodium(III) chloride ( $\text{RhCl}_3$ ), in an amount corresponding to 1.0 wt% Rh metal. The mixture was stirred and heated in a water bath at approximately  $85^\circ\text{C}$ . After equilibration, the suspension was filtered, and the resulting filter cake was thoroughly washed with distilled water to remove residual chloride ions. The solid was then dried under vacuum for 1 h to obtain the  $\text{Rh}^{3+}/\text{TiO}_2$  sample. The complete adsorption of  $\text{Rh}^{3+}$  onto the  $\text{TiO}_2$  surface was confirmed by analyzing the filtrate using



inductively coupled plasma atomic emission spectroscopy (ICP-OES, Thermo Fisher Scientific Inc., iCAP7600D), which detected no remaining  $\text{Rh}^{3+}$  in the solution. To modify the structure of the  $\text{Rh}^{3+}$  species on the  $\text{TiO}_2$  surface, the  $\text{Rh}^{3+}/\text{TiO}_2$  samples were subjected to post-calcination at various temperatures ( $T_2$ ) for 1 h. This thermal treatment converted the highly dispersed  $\text{Rh}^{3+}$  species into  $\text{RhO}_x$  species on the  $\text{TiO}_2$  surface. The resulting photocatalysts are denoted as  $\text{RhO}_x/\text{TiO}_2(T_1\text{--}T_2)$ , where  $T_1$  and  $T_2$  represent the pre- and post-calcination temperatures, respectively. For example, the sample pre-calcined at 500 °C and post-calcined at 400 °C is referred to as  $\text{RhO}_x/\text{TiO}_2(500\text{--}400)$ .

### 2.3 Platinization of $\text{RhO}_x/\text{TiO}_2$

Colloidal Pt nanoparticles were prepared according to the method reported by Frens.<sup>17</sup> An aqueous solution of hexachloroplatinic(IV) acid ( $\text{H}_2\text{PtCl}_6$ , 0.0402 g  $\text{cm}^{-3}$ , 750  $\text{cm}^3$ ) was mixed with 100  $\text{cm}^3$  of an aqueous sodium citrate solution (39 mmol  $\text{dm}^{-3}$ ). The mixture was heated to boiling and maintained at reflux for 1 h. As the reaction proceeded, the solution color changed from yellow to deep gray, indicating the formation of Pt nanoparticles. Boiling was continued for an additional 30 min to ensure complete reduction. After cooling to room temperature, 50  $\text{cm}^3$  of Amberlite MB-1 ion exchange resin (ORGANO) was added to the solution to remove excess sodium citrate. After 1 h of treatment, the resin was removed by filtration using a glass filter. Pt loading onto the  $\text{RhO}_x/\text{TiO}_2$  samples was carried out *via* the colloid salting-out (CS) method.<sup>18</sup> A typical preparation of  $\text{RhO}_x/\text{TiO}_2$  loaded with 0.5 wt% Pt is described as follows:  $\text{RhO}_x/\text{TiO}_2$  powder (150 mg) was suspended in 20  $\text{cm}^3$  (0.754 mg) of the prepared colloidal Pt solution and stirred at room temperature for 30 min in a centrifuge tube. Then, approximately 1 g of ammonium chloride was added to the mixture, which was stirred for an additional 30 min to induce deposition of the Pt nanoparticles onto the  $\text{TiO}_2$  surface. The resulting solid was collected, washed thoroughly with distilled water to remove residual salts, and air-dried. The final platinized photocatalysts are denoted as  $\text{RhO}_x/\text{TiO}_2(T_1\text{--}T_2)\text{--Pt}(Y)$ , where  $Y$  represents the Pt loading (*e.g.*, 0.5 wt%).

### 2.4 Characterization

Diffuse reflectance spectra of the  $\text{RhO}_x/\text{TiO}_2$  samples were recorded using a UV-visible spectrophotometer (UV-2600, Shimadzu, Kyoto) equipped with a diffuse reflectance accessory (ISR-2600Plus, Shimadzu). The morphology of the samples was examined by transmission electron microscopy (TEM) using a JEOL JEM-2100F microscope operated at 200 kV at the Joint Research Center (JRC) of Kindai University. Rhodium K-edge X-ray absorption fine structure (XAFS) measurements were conducted in transmission mode at beamline BL01B1 of the SPring-8 synchrotron radiation facility (Hyogo, Japan). Standard data processing procedures, including background subtraction and normalization, were

performed using Athena<sup>19</sup> (version 0.9.26). Powder X-ray diffraction of  $\text{TiO}_2$  was recorded on a MiniFlex (Rigaku, Tokyo, Japan) in the JRC at Kindai University using  $\text{CuK}\alpha$  radiation with a monochromator.

### 2.5 Hydrogen formation by dehydrogenation of 2-propanol

In this study, the dehydrogenation of 2-propanol, *i.e.*, producing hydrogen ( $\text{H}_2$ ) and acetone, was selected as a model reaction under visible light irradiation, as shown in eqn (1):



Dried photocatalyst powder (50 mg) was suspended in 5  $\text{cm}^3$  of 2-propanol, degassed by bubbling with Ar, and sealed with a rubber septum. The suspension was then irradiated under visible light using a 500 W xenon (Xe) lamp (Eagle Engineering, Tokyo) equipped with a Y-43 cutoff filter (HOYA Corporation, Tokyo), while magnetically stirred in a water bath maintained at 25 °C. The amount of  $\text{H}_2$  generated in the gas phase was measured using a Shimadzu GC-8A gas chromatograph equipped with an MS-5A column. Acetone produced in the liquid phase was quantified using a Shimadzu GC-2025 gas chromatograph fitted with a DB-WAX column, with toluene used as an internal standard.

## 3. Results and discussion

### 3.1 Characterization of samples

Fig. 2 shows the UV-vis absorption spectra of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{--Pt}(0.5)$ ,  $\text{RhO}_x/\text{TiO}_2(500\text{--}400)$ , and  $\text{RhO}_x/\text{TiO}_2(500\text{--}400)\text{--Pt}(0.5)$  samples. The unmodified  $\text{TiO}_2$  exhibited absorption only below 400 nm, consistent with its intrinsic bandgap excitation. Upon deposition of Pt particles,  $\text{TiO}_2\text{--Pt}(0.5)$  showed a baseline increase in photoabsorption, typically accompanied by a visible color change from white to gray. The  $\text{RhO}_x/\text{TiO}_2(500\text{--}400)$  sample displayed additional absorption in the 400–600 nm range, attributed to the presence of  $\text{Rh}_2\text{O}_3$  nanoparticles.<sup>10</sup> In the  $\text{RhO}_x/\text{TiO}_2(500\text{--}400)\text{--Pt}(0.5)$  sample, both  $\text{RhO}_x$  and Pt contributed to enhanced photoabsorption, resulting in a broader and more

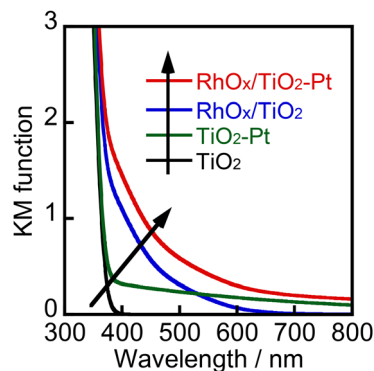


Fig. 2 UV-vis diffuse reflection spectra of various samples.



intense absorption profile. Fig. S1 (SI) presents a TEM image and particle size distribution of the colloidal Pt particles, indicating an average particle diameter of 2.9 nm with a relatively narrow size distribution (standard deviation: 1.1 nm). Fig. S2 (SI) shows a TEM image of the  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  sample prepared *via* the CS method using a Pt colloidal solution. Pt particles were clearly observed on the  $\text{TiO}_2$  surface, with an average diameter of 2.8 nm, closely matching the original size of the colloidal Pt particles prior to loading (Fig. S1, SI).

### 3.2 Formation of $\text{H}_2$ by dehydrogenation of 2-propanol

The photocatalytic activity of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-Pt}(0.5)$ ,  $\text{RhO}_x/\text{TiO}_2(500-400)$ , and  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  was evaluated for  $\text{H}_2$  production *via* the dehydrogenation of 2-propanol under visible light irradiation. The experiments were conducted at 25 °C using an Xe lamp equipped with a Y-43 cutoff filter. The spectrum of the light from the Xe lamp with the Y-43 cut-off filter used for this reaction is shown in Fig. S3 (SI). The resulting  $\text{H}_2$  generation rates for the various photocatalysts are presented in Fig. 3. No  $\text{H}_2$  evolution was observed for  $\text{TiO}_2$  or  $\text{TiO}_2\text{-Pt}(0.5)$ . This result is expected, as the Y-43 cutoff filter blocks UV light, preventing bandgap excitation of  $\text{TiO}_2$ , and the thermal catalytic activity of Pt is negligible under these conditions. In contrast, the  $\text{RhO}_x/\text{TiO}_2(500-400)$  sample generated  $\text{H}_2$  at a rate of  $1.3 \mu\text{mol h}^{-1}$ , demonstrating visible-light-driven photocatalytic activity due to the presence of Rh species. Notably, the  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  sample showed a significantly enhanced  $\text{H}_2$  production rate of  $2.8 \mu\text{mol h}^{-1}$ , indicating that Pt particles effectively function as co-catalysts for  $\text{H}_2$  evolution in this system. To confirm that this reaction proceeds *via* photocatalysis and not thermocatalysis, the  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  sample was also tested under dark conditions at 25 °C. As shown in Fig. 3, no  $\text{H}_2$  was detected, confirming that thermal dehydrogenation of 2-propanol is negligible at this

temperature. To further evaluate the roles of Rh species and Pt particles, separate samples of  $\text{RhO}_x/\text{TiO}_2(500-400)$  and  $\text{TiO}_2(500)\text{-Pt}(0.5)$  (25 mg each) were physically mixed and irradiated under the same conditions. The resulting  $\text{H}_2$  evolution rate was  $0.51 \mu\text{mol h}^{-1}$ , which is approximately half that of  $\text{RhO}_x/\text{TiO}_2(500-400)$  alone ( $1.3 \mu\text{mol h}^{-1}$ ). This finding highlights the importance of co-loading both Rh species and Pt particles onto the same  $\text{TiO}_2$  support to achieve synergistic enhancement and maximize photocatalytic  $\text{H}_2$  production from 2-propanol dehydrogenation.

### 3.3 Time courses of $\text{H}_2$ and acetone produced by 2-propanol dehydrogenation

Fig. 4 shows the time-dependent production of  $\text{H}_2$  and acetone during the photocatalytic dehydrogenation of 2-propanol over the  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  sample. The reaction was carried out under deaerated conditions and visible light irradiation using an Xe lamp equipped with a Y-43 cutoff filter. Immediately upon light irradiation, both  $\text{H}_2$  and acetone were generated from the suspension. As irradiation time increased, the amounts of  $\text{H}_2$  and acetone increased linearly. The formation rates were determined to be  $2.8 \mu\text{mol h}^{-1}$  for  $\text{H}_2$  and  $2.7 \mu\text{mol h}^{-1}$  for acetone. The close agreement between the production rates of  $\text{H}_2$  and acetone confirms that the dehydrogenation of 2-propanol proceeded stoichiometrically, as shown in eqn (1). To assess the photocatalyst's stability, the  $\text{RhO}_x/\text{TiO}_2\text{-Pt}$  sample was reused in repeated cycles, as shown in Fig. S4 (SI). After each cycle, the reaction mixture was purged with Ar and irradiated again under the same conditions.  $\text{H}_2$  evolution resumed without any noticeable decline in activity, even after prolonged irradiation, demonstrating the excellent durability of the catalyst. The total amount of  $\text{H}_2$  produced reached approximately  $47 \mu\text{mol}$ , which exceeds the stoichiometric

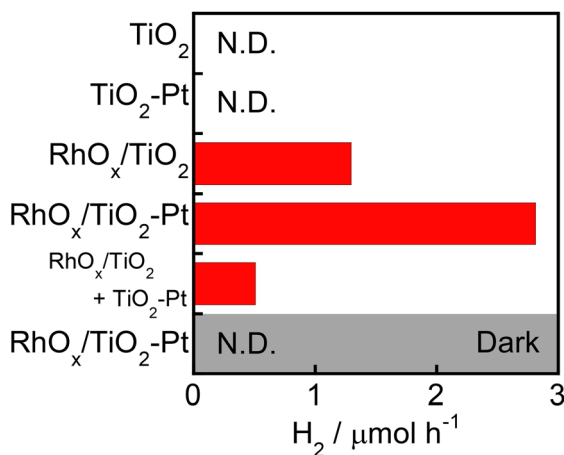


Fig. 3 Rate of  $\text{H}_2$  formation from 2-propanol suspension of various photocatalysts.

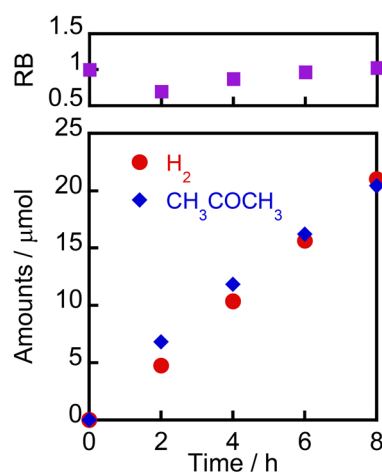


Fig. 4 Time courses of amounts of  $\text{H}_2$  and acetone in 2-propanol suspensions of  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}$  under irradiation of light from Xe lamp with cut filter Y-43.



amount of Rh present in the catalyst (4.9  $\mu\text{mol}$ , corresponding to 1.0 wt%). This clearly indicates that  $\text{H}_2$  evolution was not due to a chemical reaction between Rh species and 2-propanol, but rather was the result of a true (photo)catalytic process. The results of XPS and UV-vis for the  $\text{RhO}_x/\text{TiO}_2$ -Pt sample before and after the photocatalytic  $\text{H}_2$  formation reaction under visible-light irradiation are shown in Fig. S5 and S6 (SI). In both cases, no changes in the spectra caused by the photocatalytic reaction were observed, clearly demonstrating that the catalyst in this study was stably driven.

### 3.4 Effect of post-calcination temperature ( $T_2$ )

The structure of rhodium species was altered by varying the post-calcination temperature ( $T_2$ ), and its effect on the photocatalytic dehydrogenation of 2-propanol was investigated. Fig. 5a shows the UV-vis diffuse reflectance spectra of  $\text{RhO}_x/\text{TiO}_2(500-T_2)$  samples calcined at different

temperatures. All samples exhibited visible-light absorption, with the intensity increasing as the calcination temperature rose. This enhanced photoabsorption was attributed to structural changes in the Rh species immobilized on the  $\text{TiO}_2$  surface, rather than modifications in the bulk properties of the  $\text{TiO}_2$  support caused by calcination. In the case of  $\text{Rh}^{3+}/\text{TiO}_2(500)$  without post-calcination, previous studies have shown that Rh species exist as surface complexes coordinated to  $\text{TiO}_2$  surface hydroxyl groups, hydroxide ions, and water molecules. The positive charge of  $\text{Rh}^{3+}$  is balanced by these surface groups, including terminal oxygen atoms and hydroxyls on the  $\text{TiO}_2$  surface.<sup>10</sup> During post-calcination, coordinated hydroxide ions and water molecules are gradually removed, which is believed to enhance the interaction between Rh species and the  $\text{TiO}_2$  surface. This improved interaction likely facilitates more effective charge transfer between the Rh species and  $\text{TiO}_2$ , leading to stronger visible-light absorption. The formation of  $\text{Rh}_2\text{O}_3$  nanoparticles due to Rh species aggregation during calcination is also considered a plausible contributor to this absorption enhancement. To investigate changes in the electronic structure of Rh species, XAFS measurements were performed. Fig. 5b presents the Rh K-edge XANES spectra of commercial Rh foil,  $\text{Rh}_2\text{O}_3$ , and both uncalcined and calcined  $\text{RhO}_x/\text{TiO}_2$  samples. The spectra of  $\text{Rh}^{3+}/\text{TiO}_2$  and  $\text{RhO}_x/\text{TiO}_2(500-T_2)$  were similar to that of  $\text{Rh}_2\text{O}_3$ , but clearly different from that of Rh foil. The absorption edge energies of both uncalcined and post-calcined samples closely matched that of  $\text{Rh}_2\text{O}_3$ , indicating that the Rh species predominantly remained in the trivalent oxidation state. Fig. 5c shows  $\text{H}_2$  production rates from 2-propanol dehydrogenation using platinized  $\text{RhO}_x/\text{TiO}_2(500-T_2)$  samples. In all cases,  $\text{H}_2$  was generated, and the yield increased with increasing  $T_2$  up to 400  $^\circ\text{C}$ . The sample calcined at 400  $^\circ\text{C}$  exhibited the highest activity, producing 8.4  $\mu\text{mol}$  of  $\text{H}_2$  after 3 h. This improvement in photocatalytic activity is attributed to the enhanced visible-light absorption associated with structural changes in Rh species. However, at calcination temperatures above 400  $^\circ\text{C}$ ,  $\text{H}_2$  production decreased, likely due to excessive aggregation of Rh species, which reduces the active surface area and impairs charge transfer efficiency.

### 3.5 Action spectrum

The action spectrum has become increasingly important in the study of visible-light-responsive photocatalysis, as it represents the efficiency of light utilization as a function of wavelength. This metric is critical for identifying both the effective wavelength range and the underlying photoactivation mechanisms in a given photocatalytic system. To evaluate the action spectrum of the current system, 2-propanol dehydrogenation over  $\text{RhO}_x/\text{TiO}_2(500-400)$ -Pt(0.5) was conducted at 25  $^\circ\text{C}$  under monochromatic visible light irradiation. Light was provided by an Xe lamp equipped with a monochromator (bandwidth  $\pm 10$  nm). The

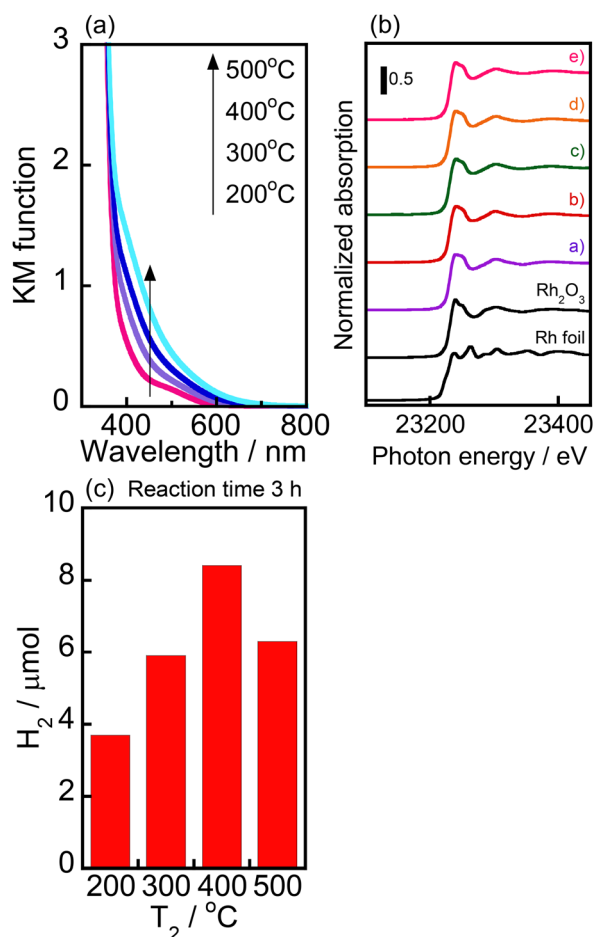


Fig. 5 (a) UV-vis diffuse reflection spectra of  $\text{RhO}_x/\text{TiO}_2(500-T_2)$ , (b) Rh K-edge XANES spectra of Rh foil,  $\text{Rh}_2\text{O}_3$ , a)  $\text{Rh}^{3+}/\text{TiO}_2$ , b)  $\text{RhO}_x/\text{TiO}_2(500-200)$ , c)  $\text{RhO}_x/\text{TiO}_2(500-300)$ , d)  $\text{RhO}_x/\text{TiO}_2(500-400)$  and e)  $\text{RhO}_x/\text{TiO}_2(500-500)$  and (c) amounts of  $\text{H}_2$  in 2-propanol suspensions of  $\text{RhO}_x/\text{TiO}_2(500-T_2)$ -Pt(0.5) under irradiation of light from Xe lamp with cut filter Y-43 for 3 h.





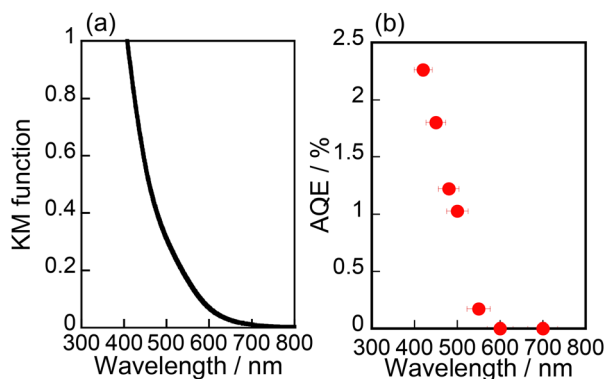


Fig. 6 (a) UV-vis diffuse reflection spectra of  $\text{RhO}_x/\text{TiO}_2(500-400)$ , and (b) action spectrum of  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}$  in formation of  $\text{H}_2$  from 2-propanol.

apparent quantum efficiency (AQE) at each central wavelength was calculated using eqn (2), which relates the rate of  $\text{H}_2$  formation to the photon flux:

$$\text{AQE} = \frac{\text{rate of } \text{H}_2 \text{ formation}}{\text{rate of incident photons}} \times 100 \quad (2)$$

The results are shown in Fig. 6. The AQE values as a function of wavelength for  $\text{RhO}_x/\text{TiO}_2\text{-Pt}$  closely matched those for  $\text{RhO}_x/\text{TiO}_2$ , indicating that  $\text{H}_2$  evolution was primarily driven by photoabsorption associated with Rh species on the  $\text{TiO}_2$  surface. These results confirm that the  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  photocatalyst is active under visible light irradiation up to 550 nm, consistent with the visible-light absorption properties introduced by the Rh species.

### 3.6 Effect of physical properties of $\text{TiO}_2$ and the amount of Pt co-catalyst

The effect of pre-calcination temperature ( $T_1$ ) on the catalytic performance of  $\text{RhO}_x/\text{TiO}_2(T_1-400)\text{-Pt}(0.5)$  was investigated. Pre-calcination influences the physical properties and crystal structure of the  $\text{TiO}_2$  support. The XRD patterns of  $\text{TiO}_2$  samples calcined at different temperatures are shown in Fig. S7 (SI). All the diffraction patterns for the samples calcined

in the 400–800 °C range were characteristic of the anatase  $\text{TiO}_2$  phase (JCPDS No. 21-1272). Table 1 summarizes the  $\text{H}_2$  yields after 3 h of visible light irradiation, along with the specific surface area and crystalline phase of  $\text{TiO}_2$  prior to  $\text{Rh}^{3+}$  modification. All samples showed measurable  $\text{H}_2$  production, with activity generally correlating with the specific surface area of the  $\text{TiO}_2$ , regardless of its crystalline phase. Among the tested samples,  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$ , which utilized anatase-type  $\text{TiO}_2$ , exhibited the highest  $\text{H}_2$  yield of 8.4  $\mu\text{mol}$  after 3 h.

To evaluate the influence of Pt loading on the  $\text{H}_2$  evolution rate, a series of  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(Y)$  photocatalysts with varying Pt contents ( $Y$ ) were prepared. The corresponding  $\text{H}_2$  yields under visible light irradiation (after 3 h) are also shown in Table 1 (entries 1 and 5–10). The Pt-free  $\text{RhO}_x/\text{TiO}_2(500-400)$  sample produced only a small amount of  $\text{H}_2$  (1.8  $\mu\text{mol}$ ), consistent with previous results. A low Pt loading of just 0.2 wt% significantly enhanced  $\text{H}_2$  evolution (3.8  $\mu\text{mol}$ ), indicating that Pt nanoparticles function efficiently as electron sinks (reduction sites). The  $\text{H}_2$  yield continued to increase with Pt loading, reaching a maximum of 8.4  $\mu\text{mol}$  at 0.5 wt% Pt. However, further increases in Pt content ( $Y > 0.5$  wt%) resulted in decreased activity. TEM and chemical analysis of the liquid phase confirmed that all Pt particles prepared by the CS method were successfully loaded onto  $\text{TiO}_2$  without size variation. Therefore, higher Pt loadings correspond to a greater number of Pt particles, not larger particles. The decline in photocatalytic activity at Pt loadings above 0.5 wt% is attributed to increased light scattering by the excess Pt particles, which reduces the efficiency of light absorption by the active  $\text{RhO}_x/\text{TiO}_2$  component.

### 3.7 $\text{H}_2$ production by dehydrogenation of various alcohols

To explore the versatility of the  $\text{RhO}_x/\text{TiO}_2\text{-Pt}$  photocatalyst for alcohol dehydrogenation under visible light, a range of alcohols were tested as substrates. As summarized in Table 2, the  $\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$  photocatalyst was effective in promoting the dehydrogenation of various types of alcohols, including primary aliphatic alcohols (methanol, ethanol,

Table 1 Specific surface area and crystalline phase of  $\text{TiO}_2$  before the modification with  $\text{Rh}^{3+}$  and the amount of  $\text{H}_2$  produced from 2-propanol suspensions of  $\text{RhO}_x/\text{TiO}_2(T_1-400)\text{-Pt}(Y)$  under irradiation of light from Xe lamp with cut filter Y-43 for 3 h

Entry	Sample	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	Crystal structure <sup>a</sup>	$\text{H}_2$ yield/ $\mu\text{mol}$
1	$\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.5)$	89	A	8.4
2	$\text{RhO}_x/\text{TiO}_2(600-400)\text{-Pt}(0.5)$	68	A	7.2
3	$\text{RhO}_x/\text{TiO}_2(700-400)\text{-Pt}(0.5)$	40	A	5.3
4	$\text{RhO}_x/\text{TiO}_2(800-400)\text{-Pt}(0.5)$	16	A/R	2.4
5	$\text{RhO}_x/\text{TiO}_2(900-400)\text{-Pt}(0.5)$	5.6	R	0.56
6	$\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.2)$	89	A	3.8
7	$\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.3)$	89	A	5.0
8	$\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.4)$	89	A	6.1
9	$\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.6)$	89	A	6.0
10	$\text{RhO}_x/\text{TiO}_2(500-400)\text{-Pt}(0.8)$	89	A	5.0

<sup>a</sup> A: anatase, R: rutile.



**Table 2** Amounts of H<sub>2</sub> produced from various alcohol suspensions of RhO<sub>x</sub>/TiO<sub>2</sub>(500–400)–Pt(0.5) under irradiation of light from Xe lamp with cut filter Y-43 for 3 h

Entry	Alcohols	H <sub>2</sub> /μmol
1	Methanol	3.6
2	Ethanol	2.3
3	1-Propanol	3.6
4	1-Butanol	3.0
5	1-Octanol	0.33
6	2-Propanol	8.4
7	2-Butanol	6.5
8	2-Pentanol	4.8
9	Cyclohexanol	2.2
10	Benzyl alcohol	0.54
11	1-Phenylethanol	0.39
12	2-Phenylethanol	0.28

1-propanol, 1-butanol, and 1-octanol), secondary aliphatic alcohols (2-propanol, 2-butanol, and 2-pentanol), alicyclic alcohol (cyclohexanol), primary aromatic alcohols (benzyl alcohol and 2-phenylethanol), secondary aromatic alcohol (1-phenylethanol). These results demonstrate that the RhO<sub>x</sub>/TiO<sub>2</sub>–Pt photocatalyst has a broad substrate scope for visible-light-driven alcohol dehydrogenation. For example, in the case of benzyl alcohol (entry 10), 0.54 μmol of H<sub>2</sub> was generated after 3 h of irradiation. After 20 h, 3.5 μmol of H<sub>2</sub> was detected in the gas phase, while 3.6 μmol of benzaldehyde was found in the liquid phase. The close agreement between the amounts of H<sub>2</sub> and benzaldehyde confirms the stoichiometric dehydrogenation of benzyl alcohol, as described by eqn (3):



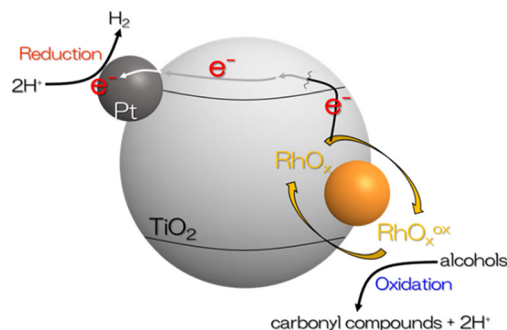
This result also indicates that benzaldehyde remained stable under the reaction conditions and was not further oxidized to benzoic acid, despite its known susceptibility to oxidation. The sustained high selectivity toward benzaldehyde highlights the mild and controlled nature of this photocatalytic process.

### 3.8 Expected reaction mechanism

Electron transfer from Rh species to the TiO<sub>2</sub> substrate under visible light irradiation has been confirmed by electrochemical measurements.<sup>8</sup> Based on these findings, the proposed mechanism for alcohol dehydrogenation, namely, the production of H<sub>2</sub> and the oxidation of alcohols, over the RhO<sub>x</sub>/TiO<sub>2</sub>–Pt photocatalyst under visible light is illustrated in Fig. 7.

The overall reaction proceeds through the following four steps:

1. Photon absorption: incident visible light is absorbed by the Rh species on the TiO<sub>2</sub> surface.
2. Electron injection: the excited Rh species inject electrons into the conduction band of TiO<sub>2</sub>.



**Fig. 7** Expected reaction mechanism for formation of H<sub>2</sub> and carbonyl compounds from various alcohols over RhO<sub>x</sub>/TiO<sub>2</sub>–Pt photocatalyst under irradiation of visible light.

3. Alcohol oxidation: the resulting electron-deficient Rh species oxidize alcohols to their corresponding carbonyl compounds and are thereby regenerated.

4. H<sub>2</sub> evolution: the injected electrons in the TiO<sub>2</sub> conduction band migrate to the Pt co-catalyst, where protons (H<sup>+</sup>) are reduced to generate molecular hydrogen (H<sub>2</sub>).

This mechanism highlights the synergistic role of Rh and Pt species: Rh serves as a visible-light sensitizer and oxidation site, while Pt acts as a reduction site for hydrogen evolution.

## Conclusions

TiO<sub>2</sub> was successfully modified through the equilibrium adsorption of Rh ions followed by post-calcination, resulting in the formation of RhO<sub>x</sub>/TiO<sub>2</sub>. The resulting photocatalyst was employed for alcohol dehydrogenation, leading to the production of H<sub>2</sub> and carbonyl compounds under visible light irradiation from an Xe lamp equipped with a Y-43 cutoff filter. The dehydrogenation rate increased significantly upon further modification of RhO<sub>x</sub>/TiO<sub>2</sub> with Pt using a colloid impregnation method. In the RhO<sub>x</sub>/TiO<sub>2</sub>–Pt photocatalyst system, TiO<sub>2</sub> serves as the support, RhO<sub>x</sub> acts as the visible-light sensitizer, and Pt functions as the co-catalyst for H<sub>2</sub> evolution. The overall reaction performance was found to depend on three key factors: the pre-calcination temperature, the post-calcination temperature, and the Pt loading. Optimal conditions were identified for each parameter. Among the tested compositions, RhO<sub>x</sub>/TiO<sub>2</sub>(500–400)–Pt(0.5), based on anatase-phase TiO<sub>2</sub>, exhibited the highest H<sub>2</sub> yield. Furthermore, the RhO<sub>x</sub>/TiO<sub>2</sub>–Pt photocatalyst demonstrated effective activity for the dehydrogenation of a range of alcohols under visible light irradiation.

## Author contributions

Atsuhiko Tanaka: conceptualization, formal analysis, writing – original draft, review & editing, supervision, funding acquisition, project administration, final approval of the article. Masaaki Fukuda: investigation, acquisition of data, analysis of data, final approval of the article. Takumi Nagai:





investigation, acquisition of data, analysis of data, final approval of the article. Hiroyuki Asakura: acquisition of data, analysis and interpretation of data, final approval of the article. Hiroshi Kominami: writing – review & editing, supervision, funding acquisition, project administration, final approval of the article.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: Fig. S1–S3 See DOI: <https://doi.org/10.1039/d5cy00963d>.

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