

Electron Source in Photoinduced Hydrogen Production on Pt-supported TiO₂ Particles

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Photoinduced reaction in relations to water photolysis was studied on Pt- or other catalysts-supported TiO₂ (P-25) particles. It was found that stoichiometric H₂ and O₂ formation does not take place with the photocatalyst, and only H₂ production was observed. A long-term water photolysis was carried out by Pt-supported TiO₂ (TiO₂/Pt) to produce H₂, in which H₂ formation stopped almost after 600 h irradiation. After recovering the TiO₂/Pt particles used in the long-term reaction, they were reused in a photocatalytic H⁺ reduction by adding methanol as an electron donor, but no H₂ production was observed showing that the TiO₂/Pt particles have lost their photocatalytic activity after the long-term reaction. These results suggest that TiO₂ itself works as an electron donor to produce H₂. Structural change of the TiO₂/Pt have been studied by both X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) before and after the photoreaction. In both the XRD and XPS, the structure of the original TiO₂ almost disappeared after the photoreaction and new structures appeared, showing that Ti⁴⁺ changed irreversibly to a higher valance state (Ti⁵⁺) after producing H₂.

Introduction

Construction of an artificial photosynthetic system is an important as well as urgent subject to obtain a new energy resource by use of solar energy and water instead of fossil fuels. TiO₂ has been considered as one of the most promising photocatalysts ever since Honda and Fujishima reported the photoelectrochemical water splitting by a TiO₂ electrode.¹ TiO₂ powders have been applied recently to remove photochemically a variety of pollutants and wastes.² Although great efforts have been made to achieve water photolysis by Pt- or metal-oxide-supported TiO₂ particles, there has been only several reports to claim stoichiometric H₂ and O₂ formation.³ However, the reproducibility of the reported systems has often been a problem. There has been a question regarding why the water photolysis by catalyst-supported TiO₂ particles is not established. In the earlier papers, the reasons have been discussed as follows; (i) progress of hydrogen spillover (the transfer of a H atom adsorbed on a Pt particle to the O₂ produced on the TiO₂ surface),⁴ and formation of the peroxo species;⁵ (ii) recombination of O₂ and H₂ to reproduce H₂O,^{3a} and (iii) contamination of TiO₂ by some organic compounds originating from the preparation,⁶ etc. Among the various types of TiO₂ particles, commercial P-25 has been known as an active photocatalyst,⁷ but the reason remains unsolved. To elucidate the photocatalytic reaction on TiO₂ particles, water photolysis was tried by Pt- or other-catalysts-supported TiO₂.

Experimental Section

Materials and Photoreaction. TiO₂ (P-25) particles were donated by the Nippon Aerosil Co. Ltd. and used as received. H₂PtCl₆, Fe(NO₃)₃, and K₂S₂O₈ were of the purest grade from

Kanto Chemical Co. Inc. Ruthenium Red (Ru-red, [(NH₃)₅Ru–O–Ru(NH₃)₄–O–Ru(NH₃)₅]⁶⁺) was purchased from Wako Pure Chemical Industries Ltd. Both IrO₂ and RuO₂ were from Aldrich Chemical Co. Ltd.

Pt-supported TiO₂ (TiO₂/Pt) was prepared by photodeposition of Pt from a H₂PtCl₆ aqueous solution onto TiO₂ without using any electron donor such as alcohol. The TiO₂ particles (1 g) were suspended in an aqueous solution (200 mL) of H₂PtCl₆ (8 mg) followed by the irradiation with a 100 W high-pressure Hg lamp (Sen Light Corp., HLR 100T-1) under air to obtain Pt-supported TiO₂ (TiO₂/Pt) after 24 h. TiO₂/Pt was also prepared by using methanol as an electron donor according to the previous work.^{3f} The obtained TiO₂/Pt (0.3 wt % Pt) was washed repeatedly with a large excess of water. The TiO₂/Pt was also prepared by simply mixing TiO₂ powders with Pt-black. Preparation of metal-oxide (RuO₂ or IrO₂)-supported TiO₂/Pt was carried out as follows: The Pt particles were first photodeposited from a PtCl₆²⁻ aqueous solution onto the TiO₂ surface, and then the metal oxide (RuO₂ or IrO₂) was loaded by simply mixing with TiO₂/Pt.

Water photolysis was carried out in pure water containing suspended TiO₂/Pt under argon using a gastight cell. All photochemical reactions were carried out under magnetic stirring. A 100 W high-pressure Hg lamp was used as a light source. The photoreaction was studied by putting the cell in a water bath during continuous water flow in the bath (about 20 °C). After the photocatalytic reaction, the gaseous product(s) formed was analyzed by a gas chromatograph (Shimadzu, GCPT-4C) with a molecular sieve 5 Å column and argon carrier gas. For some experiments more than two runs were carried out for one experiment, and the errors were ±10%.

Studies in Both X-ray Photoelectron Spectroscopy (XPS) and X-ray Powder Diffraction (XRD). An X-ray photoelectron spectrum was obtained with an Axis 165 (Kratos) using MgKα radiation as the excitation source. An X-ray diffractometer (RINT-1000, Rigaku) with CuKα radiation was employed for

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TABLE 1: Typical Results of the Photocatalytic Reaction of Water by TiO₂/Pt (0.3 wt %)^a

run	method of photodeposition of Pt onto TiO ₂	H ₂ produced/mL	O ₂ produced/mL
1 ^b	with methanol	1.80	0
2 ^c	without methanol	1.04	0

^a Reaction time, 16 h; water, 16 mL; TiO₂, 0.3 g. ^b Pt-supported TiO₂ was prepared in the presence of methanol under UV irradiation. ^c No electron donor was used for the preparation of Pt-supported TiO₂ by photodeposition.

TABLE 2: Typical Results of the Photocatalytic Reaction of Water^a

run	system	H ₂ produced/ μL	O ₂ produced/ μL
1	TiO ₂	0	0
2	TiO ₂ /Pt (0.3 wt %, mixing)	60.4	0
3	TiO ₂ /Pt (0.3 wt %, photodeposition)	552.9	0
4 ^b	TiO ₂ /Pt (0.3 wt %, photodeposition)/ adsorbed Ru-red (0.1 wt %)	82.0	0
5	TiO ₂ /IrO ₂ (0.3 wt %, mixing)	46.8	0
6	TiO ₂ /RuO ₂ (0.3 wt %, mixing)	122.3	0

^a Reaction time, 4 h; water, 16 mL; TiO₂, 0.3 g. ^b Ru-red was adsorbed after preparation of Pt-supported TiO₂ by photodeposition.

X-ray powder diffraction of the TiO₂/Pt sample before and after the photochemical reaction.

Results and Discussion

Photodeposition of Pt onto TiO₂ (P-25) particles (TiO₂/Pt) was carried out in the presence or absence of methanol as a reducing agent. Table 1 shows the results of water photolysis by the two kinds of TiO₂/Pt. Stoichiometric formation of H₂ and O₂ did not take place, and only H₂ production was observed. It was found that a much higher amount of H₂ was obtained with the TiO₂/Pt photocatalyst prepared in the presence of methanol (run 1) than with the TiO₂/Pt catalyst prepared in the absence of methanol (run 2). This indicates that trace methanol remains in the TiO₂ particles even after repeated washing, and such remaining methanol worked as an electron donor to give much more H₂. O₂ production was not achieved by the TiO₂/Pt photocatalyst prepared without any electron donor, but it should be noted that H₂ production was still achieved (run 2). O₂ production has been a problem in many of the TiO₂ photocatalyst systems. In a separate experiment, analysis of peroxide was carried out by colorimetry. However, no peroxide was detected. Sato has pointed out previously that the P-25 (TiO₂) sample is contaminated with organic impurities (e. g., oil).⁶ In the present work elemental analysis of the TiO₂ was carried out, but the result showed no carbon content. Therefore, the present photolysis results indicate the presence of some donor groups (e. g., -OH groups on the TiO₂ surface or Ti⁴⁺ ion itself) in the TiO₂. To understand the photocatalytic reaction on the TiO₂, the following study was carried out by the photocatalyst (TiO₂/Pt) prepared in the absence of methanol.

Water photolysis was studied by Pt- or other metal-oxide-supported TiO₂ suspended in water (16 mL), and the results are shown in Table 2. In all the systems only H₂ production was obtained, and O₂ production did not take place. It should be noted that the amount of H₂ differs with the preparation method used to load the metal catalyst as well as the kind of the metal. Comparing run 2 with run 3, a much higher amount of H₂ was produced when the Pt was photodeposited on the TiO₂ (run 3) than with the simple mixing of Pt with TiO₂ (run

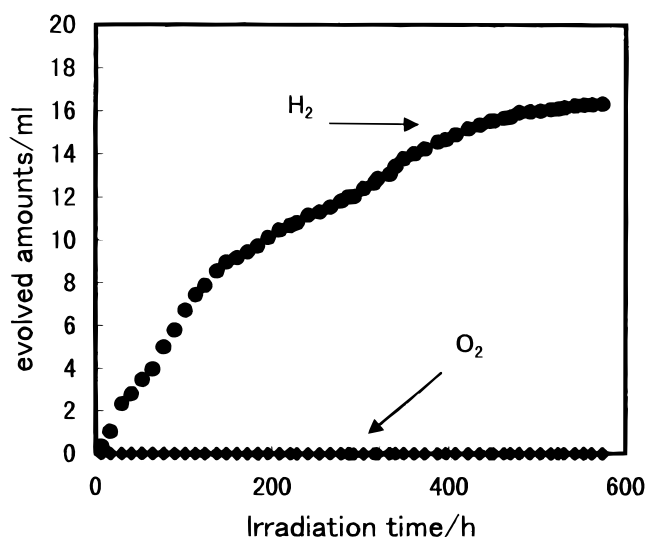


Figure 1. Time-course of the product amounts (H₂, ●; O₂, ◆) in the photocatalytic reaction of water by TiO₂(P-25)/Pt suspended in 16 mL of pure water. A 0.3 wt % Pt was loaded on TiO₂ (0.3 g).

TABLE 3: Results of Photocatalytic H⁺ Reduction in the Presence of Methanol as an Electron Donor^a

run	catalyst ^b	H ₂ produced/ μL	O ₂ produced/ μL
1 ^c	TiO ₂ /Pt (0.3 wt %) (reused)//methanol	3.6	0
2	TiO ₂ /Pt (0.3 wt %) (fresh)//methanol	577.9	0

^a Reaction time, 1.5 h; water volume, 2.7 mL including 0.1 mL methanol; TiO₂, 0.05 g. ^b Pt-supported TiO₂ was prepared by photodeposition. ^c TiO₂/Pt was recovered from the reaction mixture of long-term photoreaction (600 h) and used again in the photochemical H⁺ reduction.

2). It shows that the Pt deposited by the photogenerated electron in the TiO₂ forms more active sites to reduce H⁺. In the run 4, a trinuclear Ru complex (Ru-red) that has been found to be an active catalyst for water oxidation⁸ was adsorbed onto the TiO₂/Pt. Further, a simple mixing of other metal oxide powders (RuO₂ or IrO₂) with TiO₂ was tried in runs 5 and 6, but these results were similar to those of run 2.

A long-term photochemical reaction for water photolysis was carried out with TiO₂/Pt, and the result is shown in Figure 1. Only H₂ was produced and its formation stopped almost after the 600 h irradiation, showing that TiO₂ contains some donor groups. No example of a long-term photolysis has been reported so far.

To check the activity of the TiO₂/Pt after this long-term reaction, the TiO₂/Pt powders were recovered from the reaction mixture, washed with water, and reused as a photocatalyst by adding water containing 3.6% methanol as a reducing agent. As shown in Table 3, it was found that this catalyst no longer shows any activity (run 1) for H₂ production. Note that fresh TiO₂/Pt produced much H₂ under the same conditions (run 2). This indicates evidently that the TiO₂ itself has lost completely the activity after the long-term photoproduction of H₂, showing that the H₂ production is a sacrificial reaction.

Honda and Fujishima have reported that photoelectrochemical water splitting takes place to form O₂ on a TiO₂ electrode surface and H₂ on a counter electrode.¹ To investigate whether a water oxidation catalyst site is present on the TiO₂ powders, photocatalytic water oxidation was carried out by TiO₂/Pt in the presence of Fe³⁺ ion as an electron acceptor. The results are shown in Table 4. It was confirmed that photochemical O₂

TABLE 4: Results of Photocatalytic Water Oxidation in the Presence of Fe³⁺ Ion as an Electron Acceptor^a

run	reaction system	O ₂ produced/ μ L
1	TiO ₂ /Pt (0.3 wt %)/Fe ³⁺	552.2
2 ^b	TiO ₂ /Pt (0.3 wt %)/RuO ₂ (0.1 wt %)/Fe ³⁺	609.7
3 ^b	TiO ₂ /Pt (0.3 wt %)/IrO ₂ (0.1 wt %)/Fe ³⁺	657.8

^a Reaction time, 1 h; water, 16 mL; amount of TiO₂, 0.3 g; Fe³⁺, 0.1 M. ^b Metal oxide was mixed after preparation of Pt-supported TiO₂ by photodeposition.

TABLE 5: Results of Photocatalytic Reaction of Water in the Presence of Electron Donor or Electron Acceptor^a

run	reaction system ^b	H ₂ produced/ μ L	O ₂ produced/ μ L
1	TiO ₂ /Pt (0.3 wt %)/methanol	1117.0	0
2	TiO ₂ /Pt (0.3 wt %)/Fe ³⁺	0	46.0
3 ^c	TiO ₂ /Pt (0.3 wt %)/methanol	3.9	0
4 ^d	TiO ₂ /Pt (0.3 wt %)/Fe ³⁺ /methanol	242.7	0
5 ^e	TiO ₂ /Pt (0.3 wt %)/S ₂ O ₈ ²⁻	0	631.6
6 ^f	TiO ₂ /Pt (0.3 wt %)/methanol	596.4	0

^a Reaction time, 1 h; water, 5.0 mL including 0.1 mL methanol; TiO₂, 0.1 g. ^b Pt-supported TiO₂ was prepared by photodeposition.

^c TiO₂/Pt was recovered from the reaction mixture in run 2 and used again in the photochemical H⁺ reduction; the photocatalyst was washed with pure water several times prior to use; reaction time, 20 h. ^d Fe³⁺ ion was adsorbed from a Fe³⁺ aqueous solution; reaction time, 4 h. ^e Reaction time, 2 h. ^f TiO₂/Pt was recovered from the reaction mixture in run 5 and used again in the photochemical H⁺ reduction; the photocatalyst was washed with pure water several times prior to use.

production takes place in the presence of an acceptor, Fe³⁺, showing that there exist catalytic sites on the TiO₂ to oxidize water. Further, it was found that the addition of a metal oxide such as RuO₂ or IrO₂ as a water oxidation catalyst to the TiO₂/Pt system results in some increase of O₂ production (in the presence of Fe³⁺) showing that photochemical water oxidation takes place also on the metal-oxide catalyst sites.

It is now a question whether the activity of TiO₂ is maintained after the photocatalytic water oxidation. After carrying out photocatalytic water oxidation by TiO₂/Pt in the presence of electron acceptor such as Fe³⁺ and S₂O₈²⁻, the TiO₂/Pt photocatalyst was recovered from the reaction mixture, rinsed with a large excess of water, and reused for photocatalytic H⁺ reduction. The results are summarized in Table 5. In run 2 photocatalytic water oxidation by TiO₂/Pt was carried out in the presence of Fe³⁺ ion as an electron acceptor, which results in O₂ evolution by water oxidation. The photocatalytic H⁺ reduction by the TiO₂/Pt recovered after the run 2 reaction was carried out in the presence of methanol (run 3). However, almost no H₂ was produced. When a fresh TiO₂/Pt adsorbing Fe³⁺ was prepared and used for the photocatalytic H⁺ reduction with methanol (run 4), a much higher amount of H₂ was obtained than with the reused TiO₂/Pt photocatalyst system (run 3). However, the amount of H₂ produced in run 4 is much lower than that produced with the fresh TiO₂/Pt system in run 1. The photocatalytic activity of TiO₂/Pt would decrease by adsorption of Fe³⁺ ion onto the photocatalyst. It has been reported that adsorption of Fe³⁺ ion onto TiO₂ induces its morphological change to cause deactivation of TiO₂, and that introduction of Fe³⁺ to the TiO₂/Pt system causes formation of recombination sites by working as electron- as well as hole traps.⁹ Photocatalytic water oxidation was also carried out by using S₂O₈²⁻ as an electron acceptor (run 5). After this reaction, photocatalytic H⁺ reduction was carried out (run 6) by the recovered TiO₂/Pt used in run 5. Although the amount of H₂ in run 6 is much higher than that of the TiO₂/Pt adsorbing Fe³⁺ ion (runs 3 and 4), the photocatalytically formed H₂ by the recovered TiO₂/Pt

(runs 3 and 6) is not comparable to that of a fresh system (run 1). These series of the results in the photocatalytic reaction show that the adsorption of Fe³⁺ ion onto TiO₂ is not the only reason for the decrease of the photocatalytic activity in producing H₂. If the fresh TiO₂ sample oxidizes only water in the first runs 2 and 5, H₂ formation has to be achieved in the system using the recovered TiO₂ (runs 3 and 6). The remarkable suppression of H₂ formation shows that the TiO₂ is changed during the first O₂ evolution reaction. This change can be associated most probably with the consumption of the donor sites on the TiO₂. Therefore, the oxidations of both the water and the TiO₂ itself would take place concomitantly when the photocatalytic oxidation is carried out on the TiO₂ surface.

These photochemical characteristics of TiO₂ particles are summarized as follows. No formation of O₂ took place by conventional Pt- or metal oxide-supported TiO₂ powders without an acceptor, and only H₂ production was observed. The reason for this could be as follows. First, the possibility of the presence of a sacrificial electron donor in the TiO₂ particles must be discussed. To remove any possible impurities in TiO₂ (P-25) particles, they were extracted with hot DMF. After the extraction, TiO₂ was dried at 950 °C (24 h) under air and photodeposition of Pt particles onto the TiO₂ was carried out to study the photocatalytic reaction of water in the absence of any electron-donor agents. Comparing the photoreaction data in the treated TiO₂/Pt with a fresh one, almost similar amount of H₂ was obtained for both cases in the photocatalytic reaction of water (no production of O₂ was observed in each system). These results support the idea that photochemical H₂ production by TiO₂/Pt is not brought about by organic impurities. In the previous report, the total amount of the surface OH group was estimated as 460 μ mol/g of P-25.¹⁰ If this is applied to the present case, it is estimated under the conditions of Figure 1 that 1.4×10^{-4} mol of -OH groups are present in the 0.3 g TiO₂ particles. The H₂ (16 mL) produced in 600 h as shown in Figure 1 corresponds to 1.3×10^{-3} mol of -OH group if it works as a sacrificial electron-donating group. Therefore, the amount of H₂ produced far exceeds that of -OH groups in TiO₂. As described above, elemental analysis of TiO₂ showed no C atom. Therefore, these results can lead to the conclusion that TiO₂ itself works as a sacrificial electron donor to form H₂.

To investigate structural change of TiO₂/Pt by the photochemical reaction, X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were measured. Figure 2 shows the XRD patterns of the TiO₂/Pt sample. The XRD patterns before (a) and after (b) the photochemical reaction of Figure 1 are different in all the 2 θ angle regions. The shorter *d* spacing of the TiO₂ after the photoreaction than a fresh one as confirmed by this XRD study shows that the structural change of the TiO₂, most probably oxidation of Ti⁴⁺ to Ti⁵⁺, is induced by the photoreaction.

Figure 3 shows the XPS spectrum for Ti 2p_{3/2} before (a) and after (b) the photochemical reaction of Figure 1. In Figure 3a, a peak for Ti 2p_{3/2} of fresh TiO₂/Pt is present at 458.4 eV, corresponding to the reported value of TiO₂.¹¹ In the XPS spectrum after the photochemical reaction, the peak of Ti 2p_{3/2} (459.1 eV) is shifted to higher energy than that of the fresh TiO₂. This result shows that the valence state of Ti⁴⁺ changes to Ti⁵⁺ after the photocatalytic H⁺ reduction. In this spectrum, a shoulder peak of Ti 2p_{3/2} due to Ti⁴⁺ remains after the photoreaction (Figure 3b) showing that some Ti⁴⁺ ions do not change.

As shown in Figure 4, the XPS spectrum also shows the change of the binding energy of O 1s of TiO₂ before (a) and

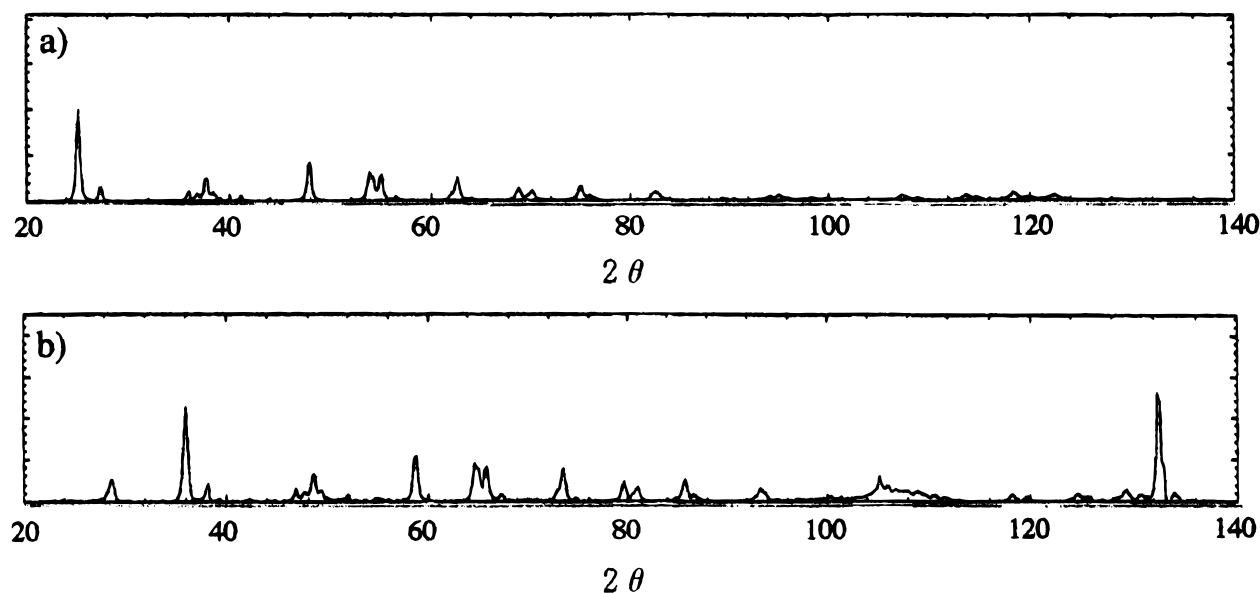


Figure 2. XRD pattern of TiO_2/Pt before (a) and after (b) photoreaction.

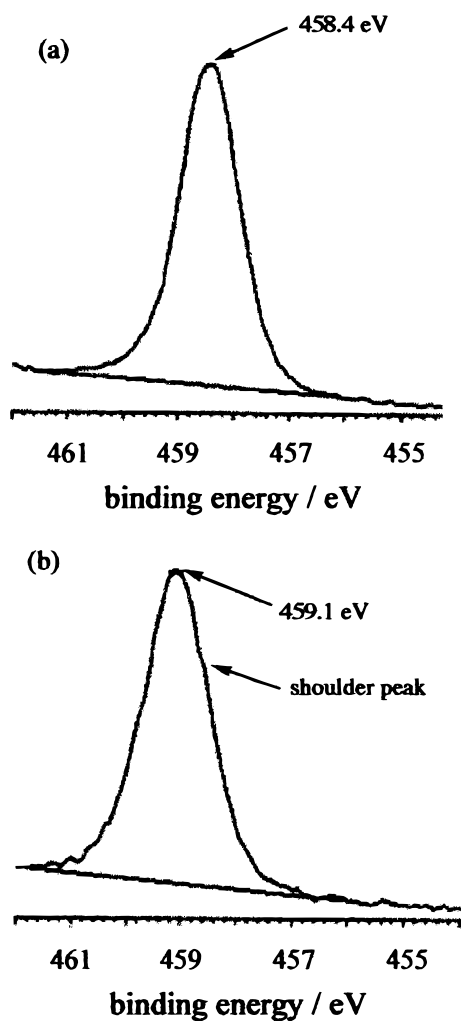


Figure 3. XPS spectra of $\text{Ti } 2p_{3/2}$ before (a) and after (b) photoreaction.

after (b) the photoreaction. The XPS signal coming from O 1s of a fresh TiO_2 is present at 529.7 eV (see Figure 4a). After the photocatalytic H^+ reduction, a doublet peak was obtained with higher binding energy than a fresh TiO_2 (the lower peak at 530.4 eV and the higher one at 532.7 eV). The peak at 530.4 eV is ascribable to O 1s of the catalyst with Ti^{5+} valent state. The

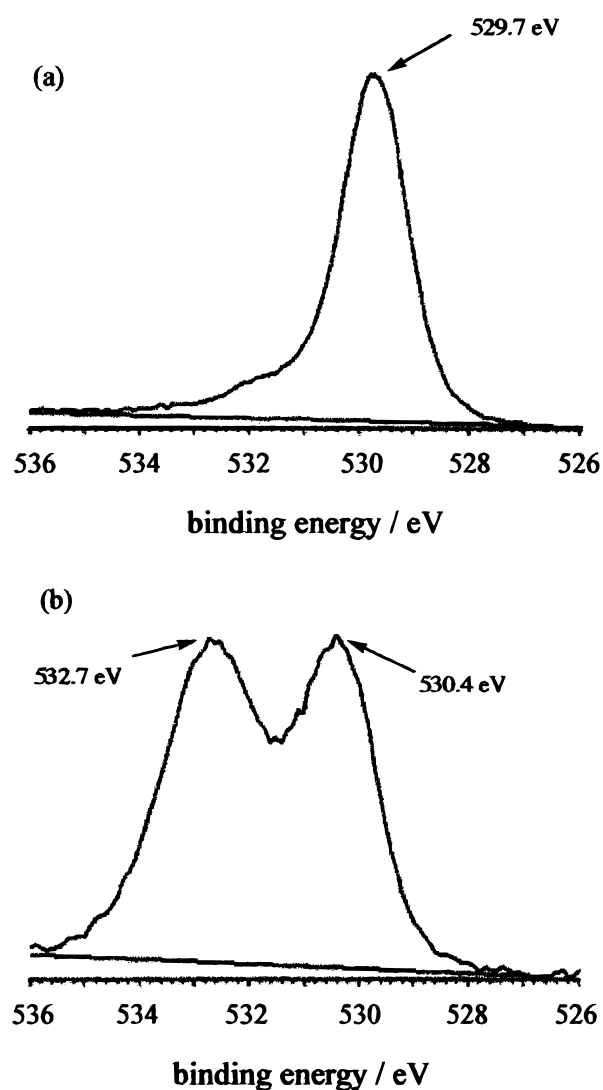


Figure 4. XPS spectra of O 1s before (a) and after (b) photoreaction. XPS signal with higher binding energy (532.7 eV) is due to O 1s of SiO_2 coming from the glass of the reaction vessel.

Thus, these H_2 production results including XRD and the XPS analysis data show that the Ti^{4+} ion has been converted to Ti^{5+}

indicating that TiO₂ itself works as an electron donor to reduce H⁺. If TiO₂ itself works as a sacrificial electron donor, 35% of the Ti⁴⁺ is calculated to change to Ti⁵⁺ after the activity is lost in the 600 h irradiation of Figure 1. It is suggested that a stable but photocatalytically inactive mixed valence structure having an average repeating unit, (Ti₂O₅)(TiO₂)₂, is formed by the photoreaction.

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