



Title	Solvothermal syntheses of semiconductor photocatalysts of ultra-high activities
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Note	Thermal treatment of titanium(IV) butoxide dissolved in 2-butanol at 573 K under autogenous pressure (alcothothermal treatment) yielded microcrystalline anatase-type titanium(IV) oxide (TiO <sub>2</sub> ). Thermal treatment of oxobis(2,4-pentanedionato-O,O')titanium (TiO(acac) <sub>2</sub> ) in ethylene glycol (EG) in the presence of sodium acetate and a small amount of water at 573 K yielded microcrystalline brookite-type TiO <sub>2</sub> . Tungsten(VI) oxide (WO <sub>3</sub> ) powders of monoclinic crystal structure with high crystallinity were synthesized by hydrothermal treatment (HTT), at 523 or 573 K, of aqueous tungstic acid (H <sub>2</sub> WO <sub>4</sub> ) solutions prepared from sodium tungstate by ion-exchange (IE) with a proton-type resin. Anatase and brookite TiO <sub>2</sub> products were calcined at various temperatures and then used for photocatalytic mineralization of acetic acid in aqueous solutions under aerated conditions and dehydrogenation of 2-propanol under deaerated conditions. Almost all the anatase-type TiO <sub>2</sub> samples showed the activities more than twice higher than those of representative active photocatalysts, Degussa P-25 and Ishihara ST-01 in both reactions. A brookite sample with improved crystallinity and sufficient surface area obtained by calcination at 973 K exhibited the hydrogen evolution rate almost equal to P-25. HTT WO <sub>3</sub> powders with various physical properties were used as photocatalyst for evolution of oxygen (O <sub>2</sub> ) from an aqueous silver sulfate solution. WO <sub>3</sub> powder of high crystallinity, e.g., IE-HTT-WO <sub>3</sub> synthesized at 573 K, gave much higher O <sub>2</sub> yield than commercially available WO <sub>3</sub> samples.
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## Solvothermal Syntheses of Semiconductor Photocatalysts of Ultra-high Activities

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### Abstract

Thermal treatment of titanium(IV) butoxide dissolved in 2-butanol at 573 K under autogenous pressure (alcoholothermal treatment) yielded microcrystalline anatase-type titanium(IV) oxide (TiO<sub>2</sub>). Thermal treatment of oxobis(2,4-pentanedionato-O,O')titanium (TiO(acac)<sub>2</sub>) in ethylene glycol (EG) in the presence of sodium acetate and a small amount of water at 573 K yielded microcrystalline brookite-type TiO<sub>2</sub>. Tungsten(VI) oxide (WO<sub>3</sub>) powders of monoclinic crystal structure with high crystallinity were synthesized by hydrothermal treatment (HTT), at 523 or 573 K, of aqueous tungstic acid (H<sub>2</sub>WO<sub>4</sub>) solutions prepared from sodium tungstate by ion-exchange (IE) with a proton-type resin. Anatase and brookite TiO<sub>2</sub> products were calcined at various temperatures and then used for photocatalytic mineralization of acetic acid in aqueous solutions under aerated conditions and dehydrogenation of 2-propanol under deaerated conditions. Almost all the anatase-type TiO<sub>2</sub> samples showed the activities more than twice higher than those of representative active

photocatalysts, Degussa P-25 and Ishihara ST-01 in both reactions. A brookite sample with improved crystallinity and sufficient surface area obtained by calcination at 973 K exhibited the hydrogen evolution rate almost equal to P-25. HTT  $\text{WO}_3$  powders with various physical properties were used as photocatalyst for evolution of oxygen ( $\text{O}_2$ ) from an aqueous silver sulfate solution.  $\text{WO}_3$  powder of high crystallinity, e.g., IE-HTT- $\text{WO}_3$  synthesized at 573 K, gave much higher  $\text{O}_2$  yield than commercially-available  $\text{WO}_3$  samples

## 1. INTRODUCTION

Titanium(IV) oxide ( $\text{TiO}_2$ ) has attracted much attention mainly in expectation of being applied to environmental photocatalytic processes such as deodorization, prevention of stains, sterilization [1], and removal of pollutants from air and water [2-4]. For the realization of their practical application, development of highly active  $\text{TiO}_2$  photocatalyst is keenly desired. Based on the kinetic investigation of photocatalytic reactions, we have pointed out that  $\text{TiO}_2$  particles having both large surface area and high crystallinity must exhibit higher photocatalytic activity [5]. The former property should increase the amount of surface-adsorbed substrate(s) to enhance the capture of photogenerated electron ( $\text{e}^-$ ) and positive hole ( $\text{h}^+$ ), and the latter, i.e., less defects acting as the recombination center, should suppress mutual  $\text{e}^-$ - $\text{h}^+$  recombination. However, it is generally difficult to satisfy these two properties by representative methods such as precipitation and sol-gel technique.

Among  $\text{TiO}_2$  there exist three crystal phases; anatase, rutile and brookite. The anatase and rutile phases are well known and many studies on their synthesis, photocatalysis and application for catalyst supports have been reported. On the other hand, only a few studies on the synthesis of brookite-type  $\text{TiO}_2$  have been examined [6,7]. To our knowledge, there is only one paper in which synthesized brookite  $\text{TiO}_2$  was successfully used as catalyst materials [8]. Difficulty to prepare brookite having both high purity and large surface is

probably one of the reasons for limited application of brookite  $\text{TiO}_2$  as catalyst support and photocatalyst.

Tungsten(VI) oxide ( $\text{WO}_3$ ), whose band gap energy has been estimated to be 2.5 eV, has the potential ability to photocatalyze under irradiation of visible light of wavelength  $<$  ca. 500 nm. Actually, visible light-induced action of oxidizing water has been reported using  $\text{WO}_3$  powder and iron(III) ions (or silver ions) as the electron acceptor [9-12]. However, commercially available  $\text{WO}_3$  powders have been used in these studies, and the properties of  $\text{WO}_3$  suitable for the photocatalytic activity for oxygen ( $\text{O}_2$ ) evolution have not been clarified. The photocatalytic  $\text{O}_2$  evolution, a half part of stoichiometric water decomposition, seem still ambiguous in its mechanism and, thereby, investigations on the visible light-induced evolution on  $\text{WO}_3$  are needed for, e.g, development of solar energy conversion systems.

In this study, we applied solvothormal method to synthesize semiconductor photocatalysts of high activities. When water ( $\text{H}_2\text{O}$ ) is used as the synthesis medium, the method is called hydrothermal method [13]. Similarly, alcohothermal means solvothormal in alcohol [14]. Here, we show solvothormal syntheses of three photocatalysts, alcohothermal synthesis of anatase-type  $\text{TiO}_2$ , solvothormal synthesis of brookite-type  $\text{TiO}_2$  in glycol- $\text{H}_2\text{O}$  medium, and hydrothermal synthesis of  $\text{WO}_3$ .

## **2. EXPERIMENTAL**

### **2.1 Alcohothermal synthesis of anatase-type $\text{TiO}_2$**

Titanium(IV) alkoxides, 10 g, was dissolved in a  $70 \text{ cm}^3$  portion of an alcohol in a test tube which was then set in a  $200\text{-cm}^3$  autoclave (Figure 1). An additional  $30 \text{ cm}^3$  of the alcohol was placed in the gap between the test tube and the autoclave wall. The autoclave was thoroughly purged with nitrogen, heated to desired temperature (523-573 K) at a rate of  $2.5 \text{ K min}^{-1}$ , and kept at that temperature for 2 h. After the autoclave treatment, the

resulting powders were washed repeatedly with acetone and dried in air.

## 2.2 Synthesis of brookite-type TiO<sub>2</sub> in glycol-water medium

Typical synthesis procedure is as follows [15]: Oxobis(2,4-pentanedionato-O,O')titanium (TiO(acac)<sub>2</sub>, 0.019 mol) (Tokyo Kasei) and sodium acetate (0.038 mol) (Kanto Chemical) were added to 70 cm<sup>3</sup> of ethylene glycol (EG) (Kanto Chemical) in a test tube, which was then set in 200 cm<sup>3</sup> autoclave. In the gap between the test tube and the autoclave wall, 5 cm<sup>3</sup> of water was added. At this point, water contacted neither TiO(acac)<sub>2</sub> nor EG. The autoclave was purged with nitrogen, heated at 573 K at a rate of 2.5 K min<sup>-1</sup>, and held at that temperature for 2 h. During the reaction, water was vaporized and dissolved in EG. The products were washed first with acetone and then with water repeatedly under sonication, and dried at room temperature.

## 2.3 Hydrothermal synthesis of WO<sub>3</sub>

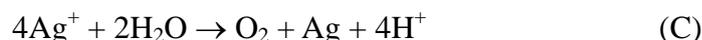
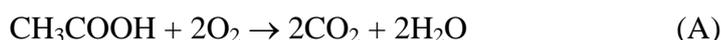
Aqueous H<sub>2</sub>WO<sub>4</sub> solutions were prepared by the cation-exchange method with a strongly acidic ion-exchange (IE) resin in its proton (H<sup>+</sup>) form [16]. Prior to IE, diluted hydrochloric acid (HCl) (0.1 mol dm<sup>-3</sup>, 240 cm<sup>3</sup>) was added to the resin (Organo, Amberlite IR120B NA, 30 cm<sup>3</sup>) packed in a glass column to make it in the H<sup>+</sup> form and then the resin was washed with distilled water until chloride ions were no longer detected in the eluent. An aqueous solution of NaWO<sub>4</sub> (Wako; 0.39 mol dm<sup>-3</sup>, 37.5 cm<sup>3</sup>) was loaded on the column and H<sub>2</sub>WO<sub>4</sub> was recovered from the column by elution with distilled water (37.5 cm<sup>3</sup>). The concentration of H<sub>2</sub>WO<sub>4</sub> solution in the elute (75 cm<sup>3</sup>) was determined to be 0.19 mol dm<sup>-3</sup>, which corresponded to 98 % recovery.

The clear H<sub>2</sub>WO<sub>4</sub> solution in the glass tube was set in a 300-cm<sup>3</sup> autoclave. The gap between the tube and inside wall of the autoclave was filled with 25 cm<sup>3</sup> of water. The

autoclave was thoroughly purged with nitrogen, heated to a desired temperature (473-573 K) at a rate of 2.5 K min<sup>-1</sup>, and kept at that temperature for 2 h. After the heating, the resulting powder was washed repeatedly with acetone and dried in air at room temperature. Hydrothermal treatment (HTT) of solid H<sub>2</sub>WO<sub>4</sub> with tungstite structure (supplied as “tungstic acid” from Kanto Chemicals) was also carried out under conditions similar to those described above.

## 2.4 Calcination and characterization

Calcination of the samples was carried out in a box furnace; the sample in a combustion boat was heated to the desired temperature at a rate of 10 K min<sup>-1</sup> and kept at that temperature for 1 h. Powder X-ray diffraction (XRD) with CuK $\alpha$  radiation was recorded on a Rigaku RINT 2500 diffractometer equipped with a carbon monochromator. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed using a Rigaku TG-8120 under a flow of air at 100 cm<sup>3</sup> min<sup>-1</sup>. Morphology of the powders was observed using a JEOL 5200 scanning electron microscope (SEM) and a JEOL JEM-3010 transmission electron microscope (TEM). Diffuse reflectance spectra were obtained by a Shimadzu UV-2400 UV-vis spectrometer equipped with a diffuse reflectance measurement unit (ISR-2000) and recorded after Kubelka-Munk analysis. Specific surface area was determined by the BET single-point method using nitrogen uptake at 77 K.



## 2.5 Photoirradiation and product analyses

(A) Photocatalytic reaction in an aqueous AcOH solution: bare TiO<sub>2</sub> powder (50 mg) was suspended in an AcOH solution (175 μmol, 5.0 cm<sup>3</sup>) [17]. (B) Photocatalytic reaction in an aqueous 2-PrOH solution: Pt (0.1 wt%)-TiO<sub>2</sub> powder (50 mg) was suspended in a 2-PrOH solution (500 μmol, 5.0 cm<sup>3</sup>) [18]. (C) Photocatalytic reaction in an aqueous silver sulfate (Ag<sub>2</sub>SO<sub>4</sub>) solution: bare TiO<sub>2</sub> powder (50 mg) was suspended in an Ag<sub>2</sub>SO<sub>4</sub> solution (125 μmol, 5.0 cm<sup>3</sup>) [19]. The reaction of (A) was carried out in reaction tubes (18 mm in diameter and 180 mm in length, transparent for light with a wavelength of > 300 nm) under aerated conditions, while those of (B) and (C) was carried out under an Ar atmosphere. The suspension was stirred (1000 rpm) at 298 K by using a magnet bar. After the irradiation, the amounts of carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>) and O<sub>2</sub> in the gas phase of reaction mixtures were measured using a Shimadzu GC-8A gas chromatograph equipped with Porapak QS (CO<sub>2</sub>) and MS-5A (H<sub>2</sub> and O<sub>2</sub>) columns. The amounts of 2-PrOH and acetone were analyzed using a Shimadzu GC-8A gas chromatograph equipped with an FID and a column packed with PEG20M. Deposited Ag was analyzed by inductively coupled plasma emission spectroscopy (ICP, Shimadzu ICPS-1000III) after dissolution with concentrated nitric acid (HNO<sub>3</sub>).

### **3. Results and Discussion**

#### **3.1 Characterization of TiO<sub>2</sub> prepared by alcohothermal method**

An XRD pattern of the product prepared by alcohothermal treatment of titanium n-butoxide (TNB) in 2-butanol at 573 K is depicted in Figure 2(a), which shows that anatase [20] was formed without contamination of any other phases such as rutile or brookite. Addition of water to the supernatant after the autoclaving gave no precipitates, indicating that TNB was completely hydrolyzed during the thermal treatment. Judging from the fact that the treatment of TNB in toluene at the same temperature yielded no product, the source of

water for the hydrolysis was that generated from 2-butanol. This sample possessed sufficient surface area of  $63 \text{ m}^2\text{g}^{-1}$  and the crystallite size of this sample was calculated to be 19 nm from the line-broadening of the 101 diffraction peak of anatase. TEM observation (Figure 3) revealed that the sample consisted of the agglomerates of primary particles of an average diameter of 20 nm, which was in good agreement with the crystallite size estimated from the XRD pattern. Therefore, each particle observed in TEM should be a single anatase crystal. TG analysis revealed that this sample showed gradual weight loss of 2.42% from 373 to 1273 K and only a very weak exothermic peak at 560 K was observed in a DTA curve due to combustion of a small amount of remaining organic moieties. Absence of sharp exothermic peak due to crystallization of anatase at around 673-773 K suggests that the product contains a negligible amount of amorphous-like phase, which is well consistent with the results of XRD and TEM. When titanium isopropoxide (TIP) was dissolved in a mixed solvent of 7 vol% 2-propanol in toluene, TIP was completely hydrolyzed to give anatase as observed in 100% 2-propanol. The amount of water required for complete hydrolysis of TIP is calculated to be 0.14 mol. Assuming that 2-propanol in toluene is completely dehydrated, the amount of water formed from the mixed solvent is estimated to be 0.064 mol, which is smaller than that necessary for the complete hydrolysis of TIP. Two possibilities might account for this; 2-propanol formed by hydrolysis of TIP was dehydrated to yield water which was then used for the hydrolysis, and/or water generated by dehydration of hydrated  $\text{TiO}_2$  was used again to hydrolyze TIP. In both processes water was recycled. In the present paper, the  $\text{TiO}_2$  sample prepared by alcohothermal method is called THyCA (Transfer Hydrolytic Crystallization in Alcohols)  $\text{TiO}_2$ .

Effect of calcination on physical properties of THyCA- $\text{TiO}_2$  prepared in the TNB-2-butanol system is shown in Figure 4. Post-calcination at temperatures lower than 973 K reduced the BET surface area slightly. This is consistent with the result that the

XRD pattern of the TiO<sub>2</sub> sample calcined at 823 K was almost identical to that before calcination, as shown in Figure 2(b). Even after calcination at 973 K, the THyCA-TiO<sub>2</sub> was composed of small anatase crystallite of 26 nm diameter (Figure 2(c)) and still possessed sufficient surface area of 45 m<sup>2</sup>g<sup>-1</sup>. Calcination at 1173 K induced partial transformation into the rutile, but the sample still predominantly consisted of the anatase crystallite (Figure 2(d)). The high thermal stability of THyCA-TiO<sub>2</sub> is interpreted by assuming that the as-prepared THyCA TiO<sub>2</sub> consists of single crystals and contains negligible amount of amorphous-like phase to be crystallized into anatase and to induce sintering of crystallites upon calcination.

### 3.2 Photocatalytic activities of THyCA-TiO<sub>2</sub>

Figure 5 shows the effect of calcination on the CO<sub>2</sub> evolution rate of THyCA-TiO<sub>2</sub> in photocatalytic mineralization of acetic acid. Uncalcined THyCA-TiO<sub>2</sub> exhibited the rate of 21.3 μmol h<sup>-1</sup> that was much larger than those of representative commercial TiO<sub>2</sub>, Degussa P-25 and Ishihara ST-01 (8.5 and 11.6 μmol h<sup>-1</sup>), which have been known to show high photocatalytic activity. Since the THyCA-TiO<sub>2</sub> powders satisfied the basic requirements for active TiO<sub>2</sub> photocatalyst, i.e., both large surface area and sufficient crystallinity, the present results can be reasonably accepted. An amorphous hydrated TiO<sub>2</sub> of quite large surface area prepared by hydrolysis under atmospheric conditions showed negligible activity (<1 μmol h<sup>-1</sup>), due to large recombination probability of photogenerated e<sup>-</sup> and h<sup>+</sup> at large number of surface defects. Calcination of THyCA-TiO<sub>2</sub> powders decreased their photocatalytic activities, suggesting that surface area, i.e., adsorptivity to toward acetic acid, is decisive factor in this reaction system.

Effect of calcination on the H<sub>2</sub> evolution rate of platinized THyCA-TiO<sub>2</sub> in photocatalytic dehydrogenation of 2-propanol in aqueous suspension is shown in Figure 6.

It should be noted that temperature dependency of the rate was different from that of mineralization of acetic acid. The rate increased with temperature until 973 K and sample obtained by calcination at that temperature exhibited a rate of  $200 \mu\text{mol h}^{-1}$ , which was much higher than that of P-25 ( $100 \mu\text{mol h}^{-1}$ ) as well as the mineralization system. This dependency suggests that balance of surface area and crystallinity, which control adsorptivity and  $e^-$ - $h^+$  recombination probability, respectively, is important in hydrogen evolution system.

### 3.3 Characterization and photocatalytic activities of brookite-type $\text{TiO}_2$

XRD pattern of the product is shown in Figure 7(a). All the XRD peaks of the product were assigned to brookite [21]. The crystallite size of this brookite sample was calculated to be 16 nm from the 121 diffraction peak using Scherrer equation. Due to the nano-crystalline property, this brookite sample had a large surface area of  $78 \text{ m}^2\text{g}^{-1}$ . In the previous paper [15], Raman spectroscopy and TEM observation revealed that the product consisted of agglomerates of brookite nano-crystals without contamination of other phases, anatase and rutile. In the TG curve of the product, weight loss was observed at the range from 473 to 773 K and total weight loss up to 1273 K was 6%. An exothermic peak was observed at 562 K in the DTA curve, which is attributed to combustion of organic moieties on the product. However, no DTA peak was observed in the high temperature region.

The brookite product was calcined at various temperatures and XRD patterns after calcination are shown in Figure 7(b)-(f). A very weak peak due to the rutile phase was observed after calcination at 823 K. Peaks of brookite became sharper after calcination at 973 K and formation of rutile  $\text{TiO}_2$  was remarkable on calcination at 1173 K. The anatase form was not observed in XRD pattern of any calcined samples, indicating that brookite directly transformed to the rutile phase. These results of XRD were consistent with those of Raman spectroscopy [15]. Calcination temperature-dependency of physical properties of

the product is shown in Figure 8. Surface area of the sample gradually decreased with the elevation in calcination temperature while crystallite size increased, indicating that crystal growth of brookite occurred along with calcination and crystallinity of brookite sample was increased.

These brookite samples of various physical properties were platinized and then used for photocatalytic dehydrogenation of 2-propanol in aqueous suspensions. Effect of calcination on the H<sub>2</sub> evolution rate is shown in Figure 9. The rate increased with temperature until 973 K and sample obtained by calcination at that temperature exhibited a rate of 104 μmol h<sup>-1</sup>, which was almost similar to that of P-25 (100 μmol h<sup>-1</sup>). It should be noted that brookite-type TiO<sub>2</sub> exhibited high photocatalytic activity if it possesses adequate physical properties. Severer calcination decreased the rate as was observed in THyCA-TiO<sub>2</sub> (Figure 5). This same dependency suggests that balance of surface area and crystallinity, which control adsorptivity and e<sup>-</sup>-h<sup>+</sup> recombination probability, respectively, is important in H<sub>2</sub> evolution system independent of the crystal structure of TiO<sub>2</sub>.

### 3.4 Photocatalytic activity of WO<sub>3</sub> synthesized by hydrothermal method

Figure 10 shows XRD patterns of the powders obtained by HTT at various temperatures of H<sub>2</sub>WO<sub>4</sub> solutions. Hydrated WO<sub>3</sub> (WO<sub>3</sub>•0.33H<sub>2</sub>O) [22] was obtained by HTT at 473 K (Figure 10(a)), while WO<sub>3</sub> with a monoclinic structure [23] was obtained at 523 K (WO<sub>3</sub>-A) (Figure 10(b)), suggesting that WO<sub>3</sub> was produced via WO<sub>3</sub>•0.33H<sub>2</sub>O during HTT. For WO<sub>3</sub>-A, the yield of WO<sub>3</sub> was estimated to be 94% on the basis of the molar amount of H<sub>2</sub>WO<sub>4</sub> in the feed. Further increase in T<sub>HTT</sub> up to 573 K and prolongation of HTT time at that temperature increased the crystallinity of WO<sub>3</sub> products (WO<sub>3</sub>-B and -C, respectively) due to the higher solubility of tungsten species in water at higher T<sub>HTT</sub> (Figures 10 (c) and (d)). As clearly shown in the XRD patterns, the intensities of 020, 200, 202, 220, 400, 402

diffraction peaks in these products increased with  $T_{\text{HTT}}$  up to 573 K, indicating that the growth of  $\text{WO}_3$  crystallite proceeded toward  $a$  and  $b$  axes, especially the  $a$  axis, under HTT conditions at 573 K. SEM photographs of  $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ ,  $\text{WO}_3\text{-A}$ ,  $\text{WO}_3\text{-B}$  and  $\text{WO}_3\text{-C}$  samples are shown in Figure 11. The  $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$  sample consisted of agglomerates of fine particles, whereas  $\text{WO}_3\text{-A}$  was composed of rectangular-shaped particles. This different morphology suggests that  $\text{WO}_3$  was formed by a dissolution-recrystallization mechanism under HTT conditions. Higher  $T_{\text{HTT}}$  and longer HTT duration accelerated particle growth of  $\text{WO}_3$ , and the length of the particle of  $\text{WO}_3$  became longer, which was consistent with the results of XRD. Another feature of  $\text{WO}_3$  particles observed in the SEM analyses is coagulation of particles by HTT of longer duration. The BET surface area ( $S_{\text{BET}}$ ) of each sample is shown in Table 1. With elevation in  $T_{\text{HTT}}$  and prolongation of HTT time,  $S_{\text{BET}}$  of  $\text{WO}_3$  decreased due to an increase in the size of primary  $\text{WO}_3$  particles.

Figure 12 shows the time course of  $\text{O}_2$  evolution from a suspension of  $\text{WO}_3\text{-B}$  particles under UV-visible light irradiation. In this system,  $\text{O}_2$  evolved linearly with irradiation time up to 20 min. The yields of  $\text{O}_2$  and photodeposited Ag after 20-min irradiation was 23 and 89  $\mu\text{mol}$ , respectively, and the  $\text{Ag}/4\text{O}_2$  ratio was 0.97, indicating that  $\text{O}_2$  evolution accompanying stoichiometric Ag deposition ( $4\text{Ag}^+ + 2\text{H}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2 + 4\text{H}^+$ ) proceeds efficiently. The rate of  $\text{O}_2$  evolution, i.e., the slope of the time-course curve, gradually decreased after 20 min. The pH of the suspension decreased with the above reaction producing  $\text{H}^+$ , and the amount of  $\text{Ag}^+$  adsorbed on photocatalyst particles decreased with lowering of pH [24,25], which accounts for the decrease in  $\text{O}_2$  evolution. The activities of the present  $\text{WO}_3$  samples were evaluated by the yields of  $\text{O}_2$  and Ag after 20-min irradiation and are listed in Table 1. All  $\text{WO}_3$  samples, including three commercial ones, tested in this study, exhibited activity, though the tungstite and  $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$  samples showed negligible activity. Among the  $\text{WO}_3$  samples listed in Table 1, the  $\text{WO}_3$  samples of high crystallinity

prepared via IE-HTT showed higher activities than those of the commercial WO<sub>3</sub> samples; WO<sub>3</sub>-B exhibited the highest activity. It has been pointed out that the crystallinity of TiO<sub>2</sub> controls the activity in photocatalytic O<sub>2</sub> evolution from an aqueous suspension of TiO<sub>2</sub> [19, 26]. The above-stated results clearly show that the same strategy of design can be applied to WO<sub>3</sub> photocatalyst for O<sub>2</sub> evolution. WO<sub>3</sub>-C synthesized with a longer period possessed higher crystallinity and was expected to show higher activity than, for example, that of WO<sub>3</sub>-B. However, this was not the case. As observed in SEM (Figure 11), WO<sub>3</sub>-C particles, unlike WO<sub>3</sub>-B particles, were strongly coagulated to give large secondary particles. It is known that grain boundaries of TiO<sub>2</sub> particles induce recombination of electron-hole pairs [27]. Coagulation of particles might produce crystal defects, at boundaries of WO<sub>3</sub> particles, acting as recombination centers of electron-hole pairs. WO<sub>3</sub>-D prepared from solid H<sub>2</sub>WO<sub>4</sub> by HTT showed a smaller O<sub>2</sub> yield than those of other HTT and commercial WO<sub>3</sub> samples. Crystallinity of the WO<sub>3</sub> powder might be insufficient for O<sub>2</sub> formation, which is supported by its relatively large S<sub>BET</sub> (8.9 m<sup>2</sup>g<sup>-1</sup>).

Photocatalytic activity was also examined with 2-h photoirradiation at a wavelength of > 420 nm using a cut-off filter. WO<sub>3</sub>-B gave 12 μmol yield of O<sub>2</sub> under visible-light irradiation, though the apparent activity was much smaller than that with UV-visible irradiation due to the large decrease in the total number of photons irradiated to WO<sub>3</sub> particles. Degussa P-25, one of the most active TiO<sub>2</sub> photocatalysts, showed negligible O<sub>2</sub> evolution (0.3 μmol) due to the larger band gap energy (3.2 eV corresponding to ca. 390 nm).

#### 4. Conclusion

Anatase and brookite-type TiO<sub>2</sub> and WO<sub>3</sub> samples were successfully synthesized by solvothermal technique. Physical properties of these semiconductors can be controlled by changing solvothermal condition and post-calcination temperature. These solvothermal

products exhibited higher or similar activities than commercial active Degussa P-25 in several photocatalytic reaction systems.

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Figure captions

**Figure 1** Reaction apparatus

**Figure 2** XRD patterns of (a)  $\text{TiO}_2$  prepared by the alcohothermal treatment of titanium n-butoxide in 2-butanol at 573 K, and (b), (c), and (d) the samples obtained by calcination of (a) at 823, 973 and 1173 K, respectively.

**Figure 3** A TEM photograph of  $\text{TiO}_2$  prepared by the alcohothermal treatment of titanium n-butoxide in 2-butanol at 573 K

**Figure 4** Effect of calcination on surface area and crystallite size of THyCA- $\text{TiO}_2$ .

**Figure 5** Effect of calcination on the  $\text{CO}_2$  evolution rate of THyCA- $\text{TiO}_2$  in photocatalytic mineralization of acetic acid.

**Figure 6** Effect of calcination on the  $\text{H}_2$  evolution rate of platinumized THyCA- $\text{TiO}_2$  in photocatalytic dehydrogenation of 2-propanol in aqueous suspension.

**Figure 7** XRD patterns of (a)  $\text{TiO}_2$  prepared by the solvothelmal treatment of  $\text{TiO}(\text{acac})_2$  in EG- $\text{H}_2\text{O}$  in the presence of sodium acetate at 573 K, and (b), (c), (d), (e) and (f) the samples obtained by calcination of (a) at 623, 823, 973, 1073 and 1173 K, respectively.

**Figure 8** Effect of calcination on surface area and crystallite size of brookite-type  $\text{TiO}_2$ .

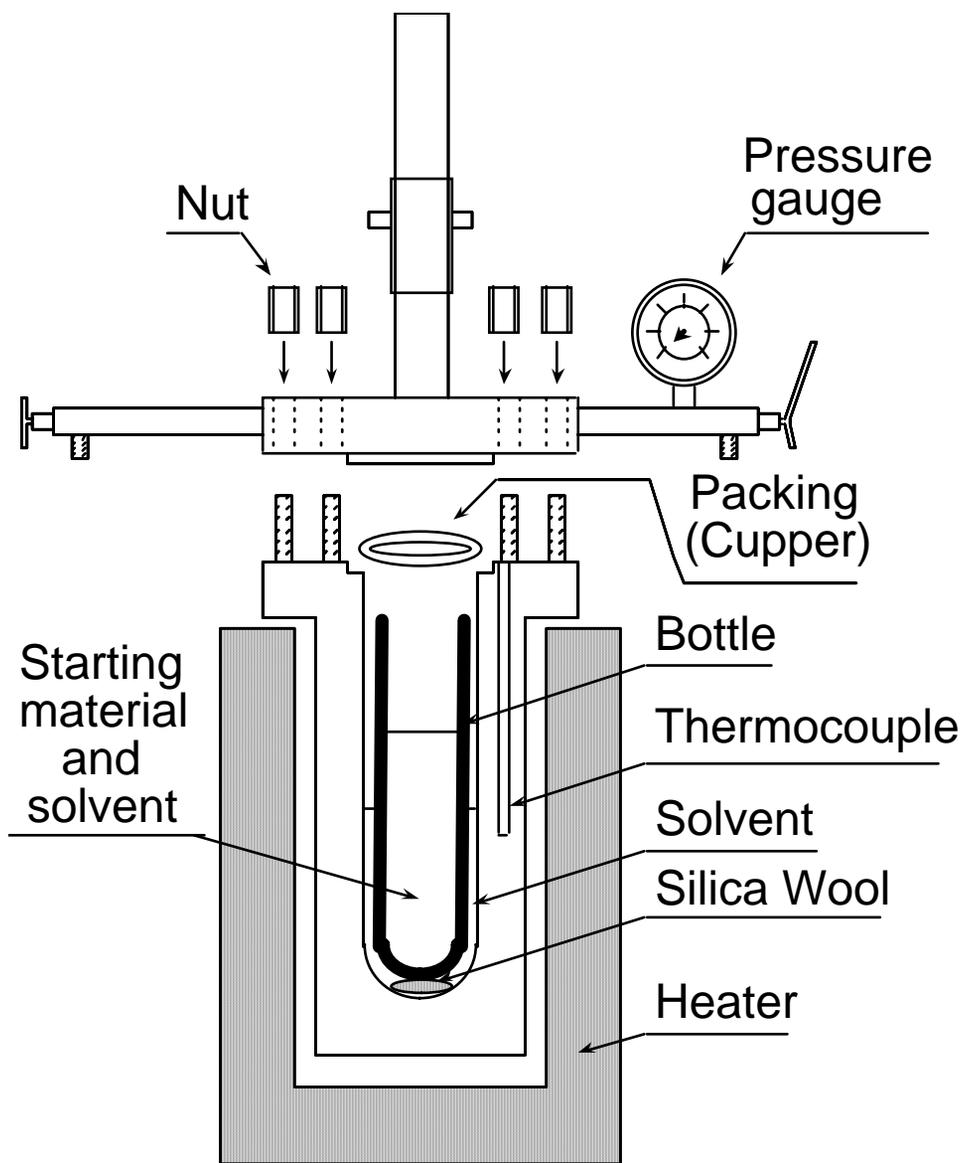
**Figure 9** Effect of calcination on the  $\text{H}_2$  evolution rate of platinumized brookite- $\text{TiO}_2$  in photocatalytic dehydrogenation of 2-propanol in aqueous suspension.

**Figure 10** XRD patterns of the compounds obtained by HTT of an  $\text{H}_2\text{WO}_4$  solution at (a) 473 K for 2 h, (b) 523 K for 2 h ( $\text{WO}_3\text{-A}$ ), (c) 573 K for 2 h ( $\text{WO}_3\text{-B}$ ), and (d) 573 K for 8 h ( $\text{WO}_3\text{-C}$ ).

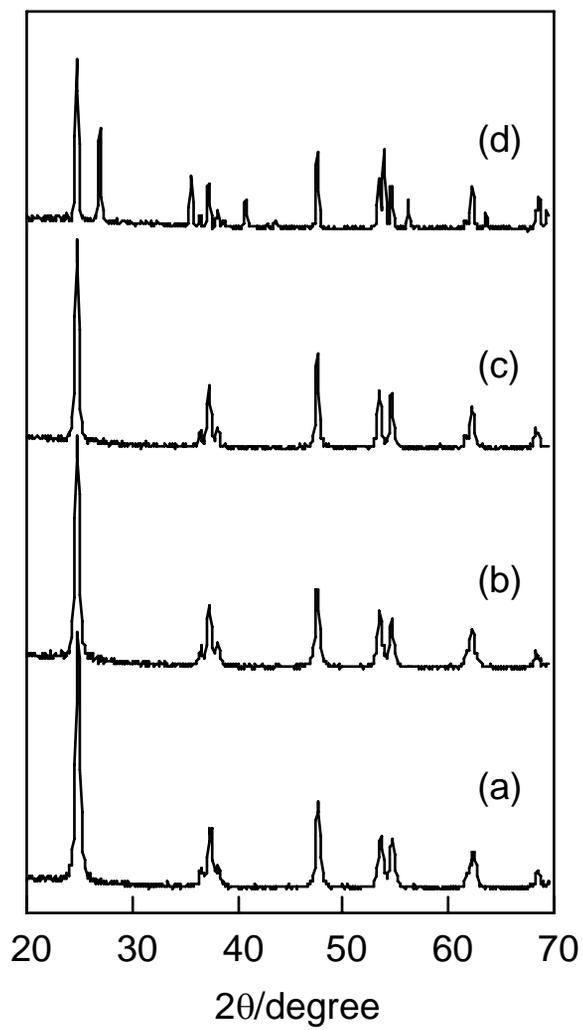
**Figure 11** SEM photographs of the compounds whose XRD patterns are shown in Figure 10.

**Figure 12** Time course of  $\text{O}_2$  evolution from  $\text{Ag}_2\text{SO}_4$  in an aqueous suspension of

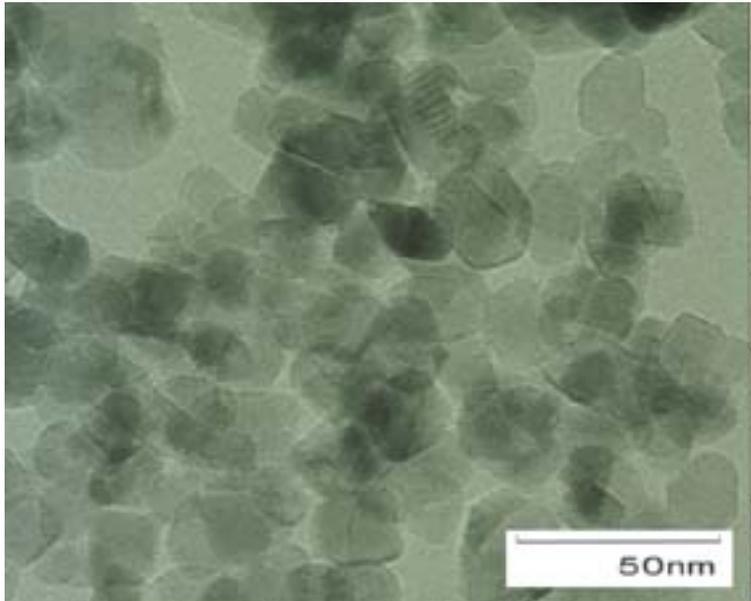
WO<sub>3</sub>-B under UV-visible light irradiation.



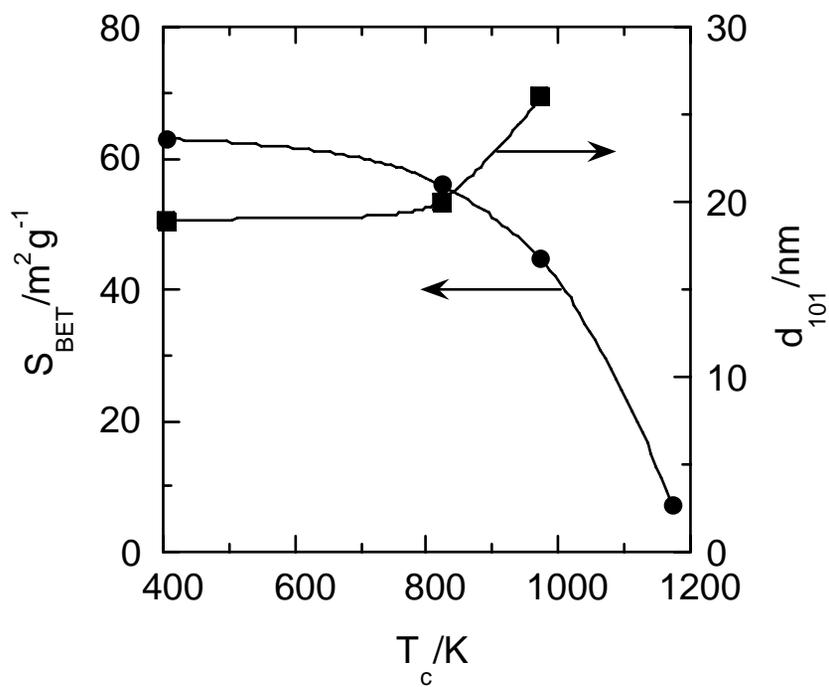
Kominami et al., Fig. 1



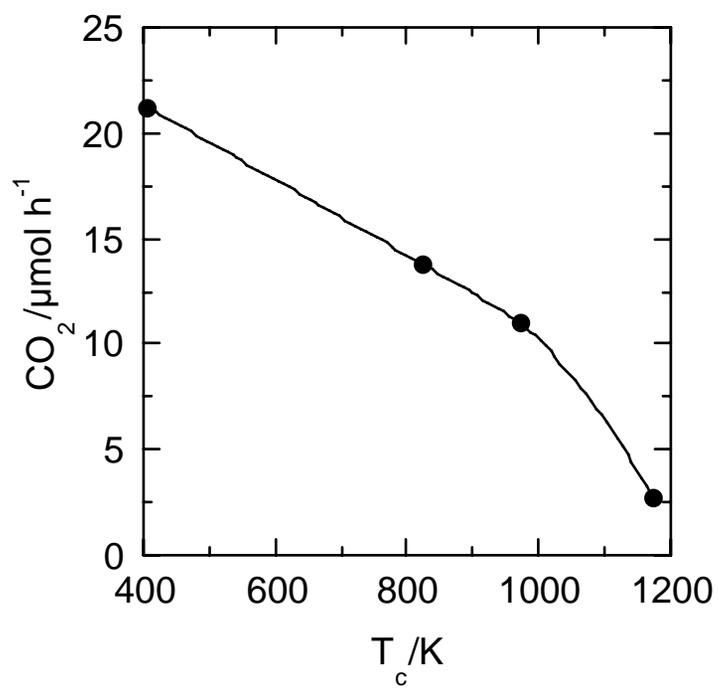
Kominami et al., Fig. 2



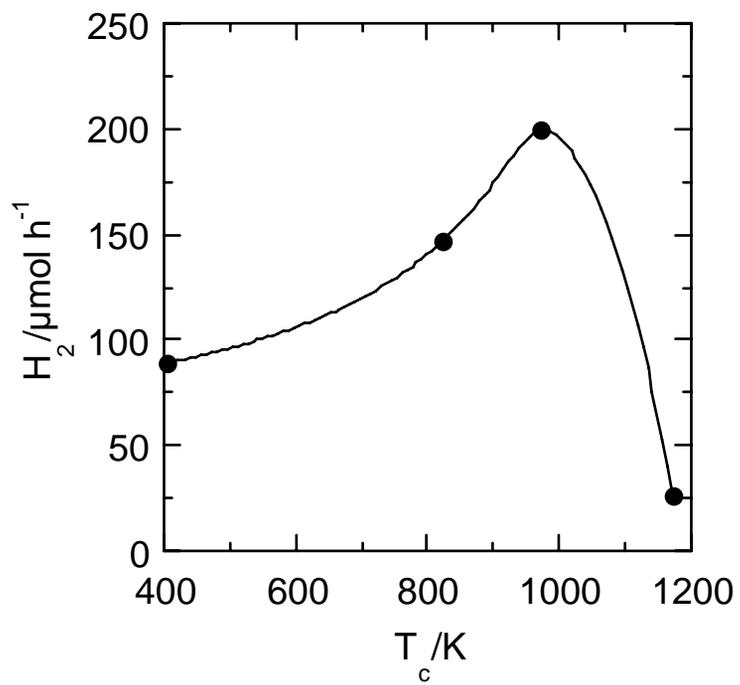
Kominami et al., Fig. 3



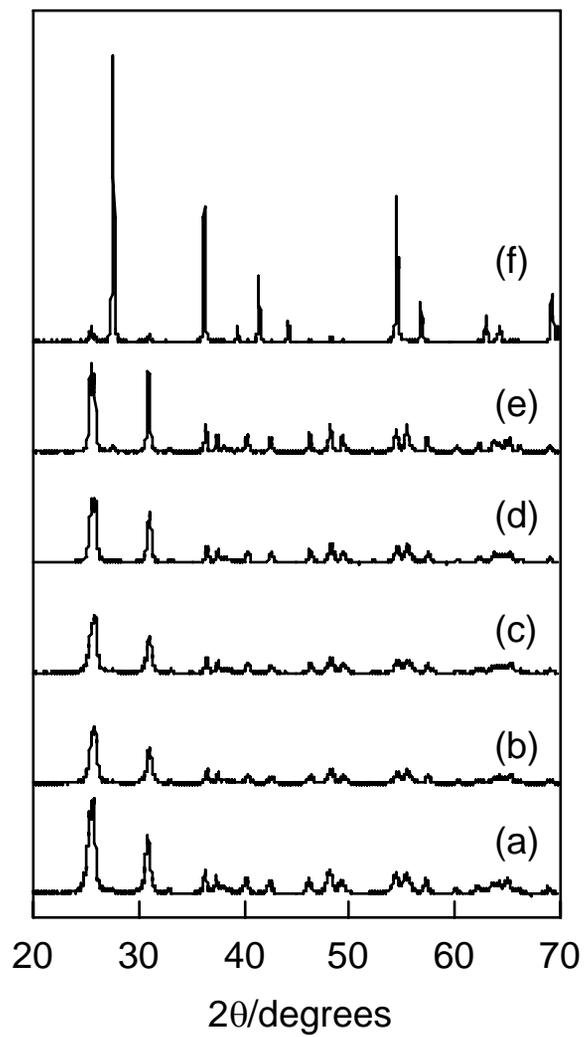
Kominami et al., Fig. 4



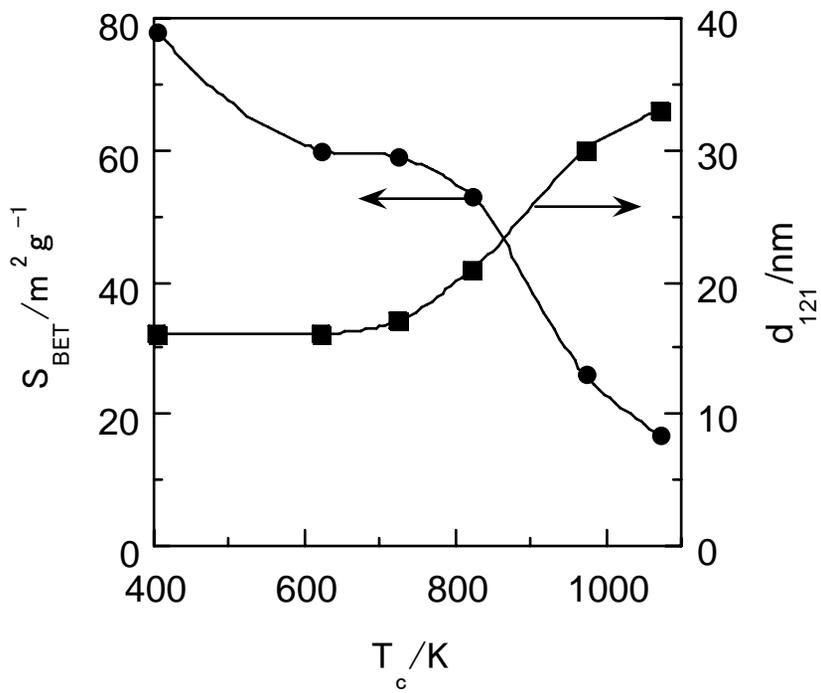
Kominami et al., Fig. 5



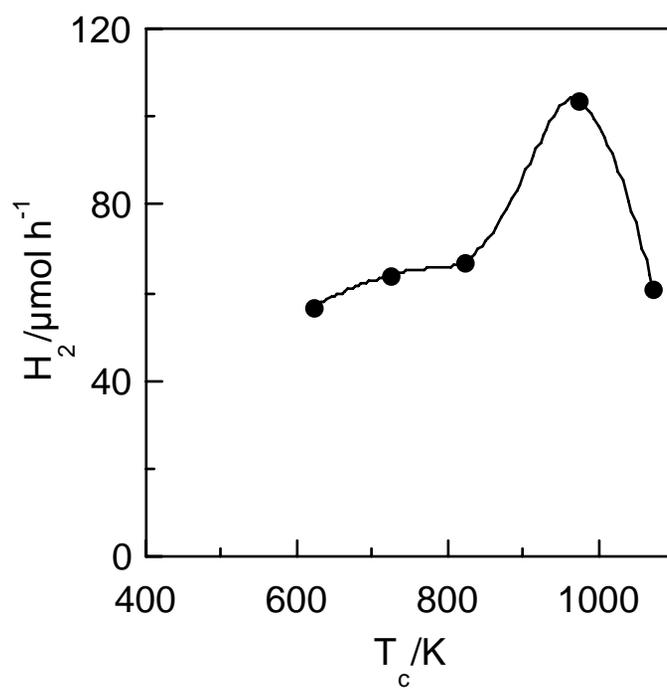
Kominami et al., Fig. 6



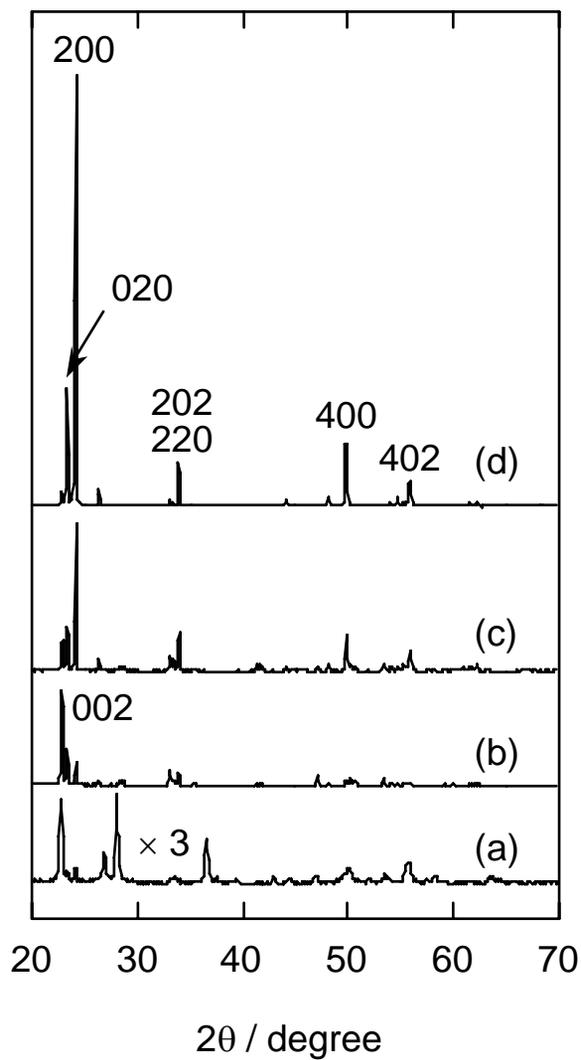
Kominami et al., Fig. 7



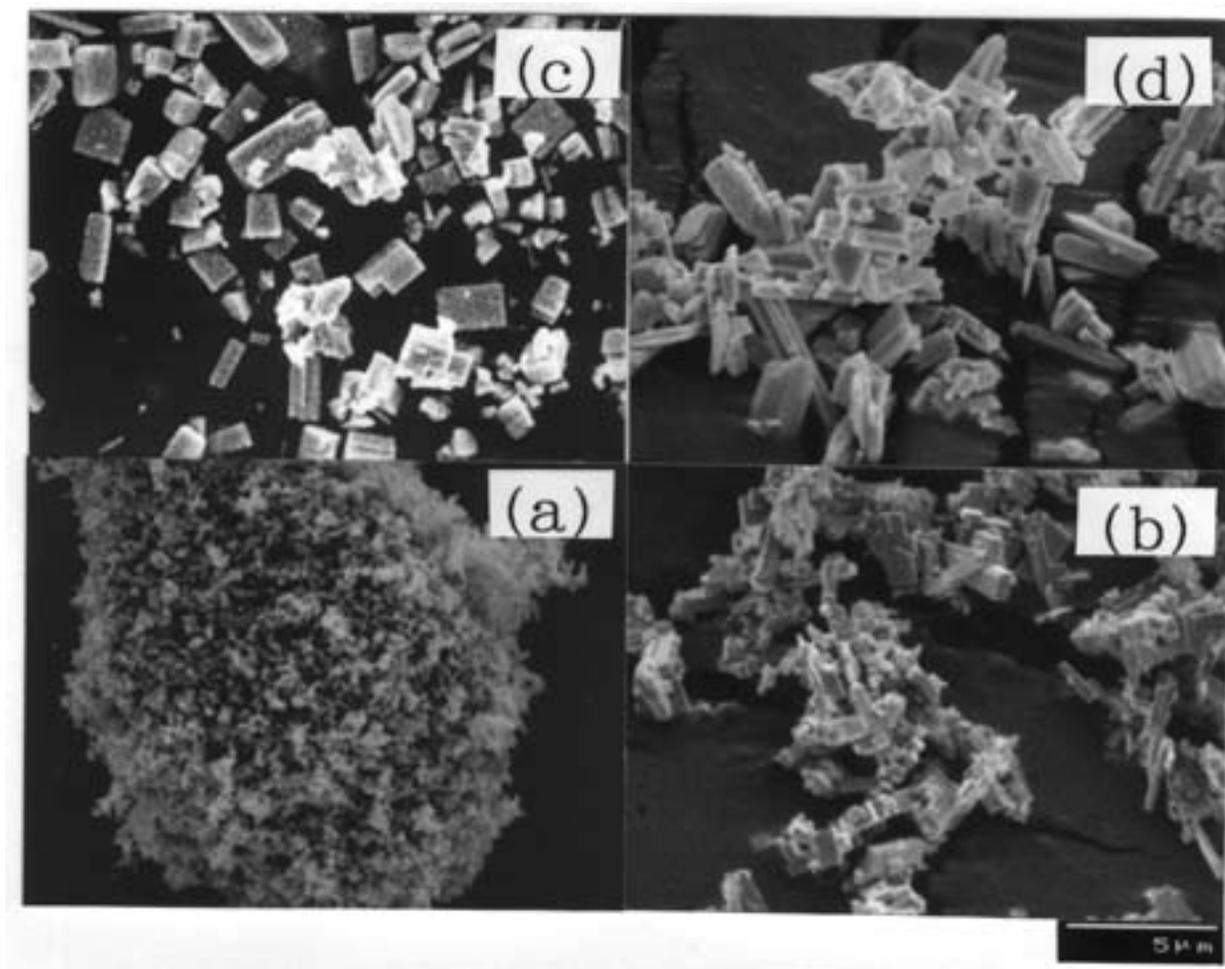
Kominami et al., Fig. 8



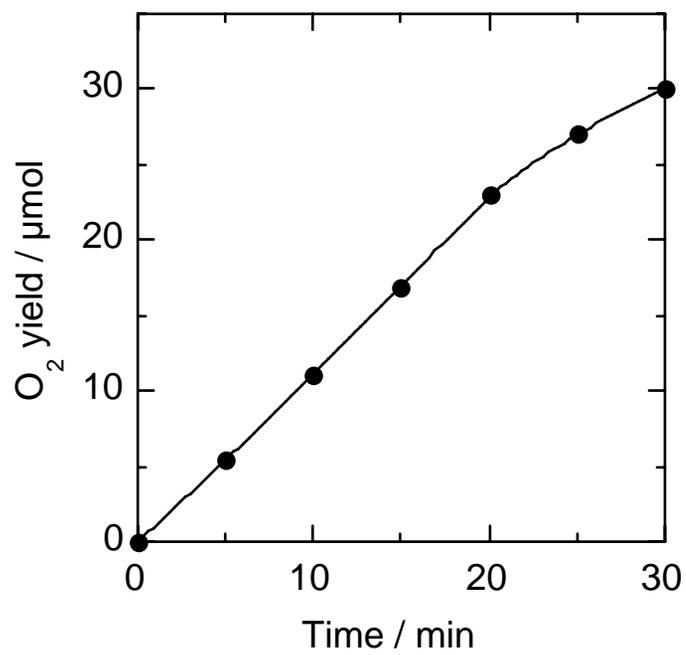
Kominami et al., Fig. 9



Kominami et al., Fig. 10



Kominami et al., Fig. 11



Kominami et al., Fig. 12

**Table 1**Photocatalytic activity (20-min irradiation) of HTT-WO<sub>3</sub> products prepared from various starting materials

sample	H <sub>2</sub> WO <sub>4</sub> material	T <sub>HTT</sub> <sup>a</sup> / K	t <sub>HTT</sub> <sup>a</sup> / h	phase	S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>	O <sub>2</sub> / μmol	Ag / μmol	Ag / 4O <sub>2</sub>
WO <sub>3</sub> •0.33H <sub>2</sub> O	solution <sup>b</sup>	473	2	orthorhombic	18	1.9	8.2	1.1
WO <sub>3</sub> -A	solution <sup>b</sup>	523	2	monoclinic	14	9.6	36	0.94
WO <sub>3</sub> -B	solution <sup>b</sup>	573	2	monoclinic	1.7	23	89	0.97
WO <sub>3</sub> -C	solution <sup>b</sup>	573	8	monoclinic	0.6	15	58	0.97
WO <sub>3</sub> -D	solid <sup>c</sup>	573	2	monoclinic	8.9	3.0	13	1.1
WO <sub>3</sub> -E <sup>d</sup>				monoclinic	3.0	11	47	1.1
WO <sub>3</sub> -F <sup>e</sup>				monoclinic	3.1	9.8	41	1.0
WO <sub>3</sub> -G <sup>f</sup>				monoclinic	5.0	6.5	25	0.96
(P-25 TiO <sub>2</sub> ) <sup>g</sup>				anatase, rutile	50	4.3	19	1.1

<sup>a</sup>Hydrothermal treatment was carried out at T<sub>HTT</sub> for t<sub>HTT</sub>.<sup>b</sup>0.19 mol dm<sup>-3</sup>, 75 cm<sup>3</sup><sup>c</sup>Supplied as tungstic acid from Kanto Chemicals.<sup>d</sup>High Purity Chemicals (99.99% purity).<sup>e</sup>Kishida Chemicals (99.9% purity).<sup>f</sup>Kanto Chemicals (99.5 % purity).<sup>g</sup>Degussa.