

Effect of TiO₂ Crystallite Diameter on Photocatalytic Water Splitting Rate

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Abstract

The effect of (Pt-loaded)TiO₂ crystallite diameter (*i.e.* Scherrer size) on the photocatalytic water splitting rate was investigated. (Pt-loaded)TiO₂ powders with a wide range of crystallite diameters from about 16 to 45 nm with a blank region between about 23 and 41 nm were prepared by various annealing processes from an identical TiO₂ powder. Water splitting experiments with these powders were carried out with methanol as an oxidizing sacrificial agent. It was found that the photocatalytic water splitting rate was sensitively affected by the crystallite diameter of the (Pt-loaded)TiO₂ powder. More concretely, similar steep improvements of photocatalytic water splitting rates from around 15 and a little over 2 to about 30 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ were obtained in the two (Pt-loaded)TiO₂ crystallite diameters ranging from 16 to 23 and from 41 to 45 nm, respectively.

Keywords

Photocatalytic Water Splitting, TiO₂ Crystallite Diameter, Scherrer Size, X-Ray Diffraction, Critical Water Anneal

1. Introduction

The primary components for photocatalytic water splitting are photocatalysts with a metal loaded for inducing the Schottky effect, water and oxidizing sacrifice agents to scavenge the coproduced oxygen gas, preventing the reverse reaction of oxygen with hydrogen to water [1]-[4]. In contrast to commonly used water-soluble oxidizing sacrifice agents such as saccharides and alcohols, previous work indicated suitability of water-insoluble cas-

tor-oil, which has the added benefit of being a nonfood natural hydrocarbon, and helps enable carbon-neutral photocatalytic water splitting [5].

Regarding photocatalysts, TiO₂ is still the most promising material due to its band structure that is especially well suited for water splitting. As band gaps of TiO₂ are 3.0 and 3.2 eV in anatase and rutile forms, their excitations require ultraviolet light of less than 400 and 380 nm in wavelength, respectively. Many have attempted to enable visible light induction in TiO₂ via doping metals or nonmetal ions [6]-[9]. However, the benefits are currently far outweighed by the complex manufacturing methods, high costs, instability issues, etc.

Our group has focused on increasing the crystallite diameter of TiO₂ powder in order to improve its quantum efficiency. Ohtani and co-workers have already reported improving photocatalytic water splitting rates by increasing crystallite diameters of anatase TiO₂ with loading Pt in 2 wt% [10], however only crystallite sizes in the range of about 20 to 30 nm and around 55 nm were studied. Since our group recently invented novel annealing processes utilizing thermo fields of sub- or super-critical water with dissolving or undissolving metal-salts [11]-[13], supplementing experiments to cover the TiO₂ crystallite size ranges, where Ohtani and co-workers could not prepare, have been ready to be performed.

In this study, TiO₂ powders with a wide range of crystallite diameters were prepared by various annealing processes from an identical starting TiO₂ powder. After Pt loading to the prepared TiO₂ powders, photocatalytic water splitting experiments were performed. Measured hydrogen producing rates were assessed with respect to the (Pt-loaded)TiO₂ crystallite diameters (*i.e.* Scherrer sizes) determined from their X-ray diffraction patterns and the Scherrer's equation [14]. Finally, future strategies for further enhancement of photocatalytic water splitting rates were discussed particularly in terms of selection of the starting TiO₂ powders and operating parameters for their annealing and Pt loading to them.

2. Experimental Apparatus and Procedures

Figure 1 shows a schematic of the experimental apparatus for photocatalytic water splitting [5]. The main reactor was made of Pyrex glass in a cylindrical shape with 90 mm internal diameter, 40 mm tall and a volume of about 255 mL. The cylinder had two taps for replacing air inside initially by Ar-gas and sampling produced-gas intermittently throughout the experiment. The top cover was made of solid quartz glass with high transmissivity toward ultraviolet rays. To maintain a constant reaction temperature, a cooling chamber was attached to the bottom of the cylinder, where water at 298 K was circulated.

The starting TiO₂ powders utilized were ST-01 (anatase form) manufactured by Ishihara Sangyo Kaisha, Ltd. Japan. First, 1.0 g of TiO₂ powder was grinded for 60 min in an automatic grinder (ANM1000, Nitto Kagaku Co., Ltd., Japan), then inserted into a 1/2-inch-SUS304 annealing tube as shown in **Figure 2** together with 3.0 mL of water and 1.0 g of NaCl, where ionic bonding metal-salts had been found to contribute to increase TiO₂ crystallite diameter in previous works [11] [12]. After dissolving the added salt, the tube was completely sealed. Before the annealing treatment, the whole tube was soaked in a water bath of an ultrasonic washing device (US-5, SND, Japan, bath volume: 20 L, ultrasonic frequency: 38 kHz, output power: 300 W), and then ultrasonic wave was irradiated for 30 min to disperse all adhering powders isolated each other inside the tube. The annealing tube was heated in an electric furnace (MMF, AS ONE, Japan) to 660 K at a constant heating rate of 6.0 K min⁻¹ and then held for 1 hr, taking into consideration the critical temperature of water at 647.3 K. The pressure inside the SUS tube was calculated to be 26.1 MPa [15], which is well above the critical pressure of water at 22.1 MPa. After these procedures, the power supply to the furnace was cut, and then the tube was spontaneously cooled down to room temperature in the furnace.

As comparative annealing treatments, following two operations were implemented. The annealing tube prepared by the same procedures mentioned in the foregoing paragraph was quickly introduced into the preheated furnace at 660 K and then quenched in a sufficiently big water bath down to room temperature after a holding time of 1 hr. And, the annealing tube involving only 1.0 g of TiO₂ powder was handled in the same thermal history described in the foregoing paragraph.

The treated TiO₂ powder was washed by de-ionized water, and dried in a vacuum oven (VO-320, Advantec Toyo Kaisha, Ltd., Japan) at 373 K for 24 hrs. And then, measurements were carried out with a laser diffraction/scattered device (LA-920, Horiba, Japan, ultrasonic frequency: 22.5 kHz, output power: 30 W) for a size distribution, and an X-ray diffraction (RINT2500TTR, Rigaku Denki, Japan) for a crystallite diameter (*i.e.* Scherrer size) calculated by the Scherrer's equation [14]. Here, size distributions of any powders utilized in this

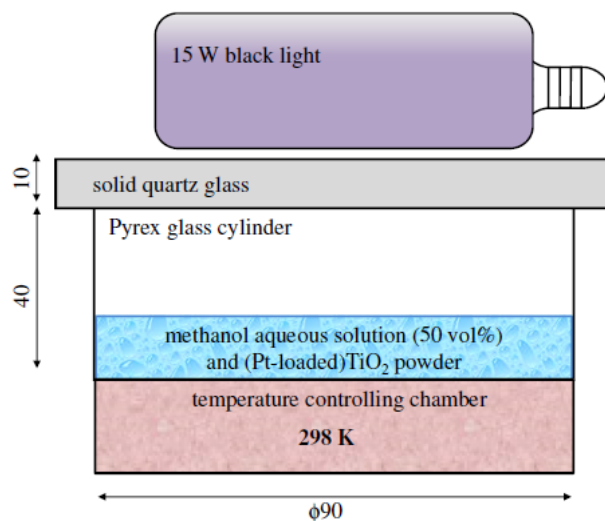


Figure 1. Schematic of experimental apparatus for water splitting.

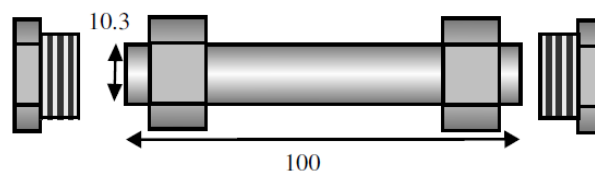


Figure 2. Schematic of annealing SUS-tube.

study were found almost the same. Then, 0.1 wt% of Pt was loaded to the TiO_2 powder by photodeposition of hexachloroplatinic acid according to preparation methods found in literatures [16] [17]. Since the crystallite diameters of TiO_2 powder before and after Pt loading were different, the crystallite diameters of the (Pt-loaded) TiO_2 powders were used for arranging and analyzing the data obtained for photocatalytic water splitting experiments.

As for the water splitting experiments, 5.0 mL of 50.0 vol% methanol solution was poured into the reactor with 0.50 g of Pt/ TiO_2 powder. Then, after replacing air inside the reactor by Ar-gas and starting the circulation of water at 298 K in the cooling chamber, the light irradiation by a black light (EFD15BLB-T, 15.0 W, Toshiba Lighting & Technology Corporation, Japan) was initiated. Finally, hydrogen concentration inside the gas phase of the reactor was periodically measured by means of TCD gas-chromatography (GC-8A, Shimadzu Corporation, Japan). Due to these procedures, experimental repeatability could be conveniently preserved.

3. Results and Discussion

3.1. Crystallite Diameters of TiO_2 Powders Due to Different Annealing Treatments

Figure 3 compares XRD patterns of the annealed TiO_2 powders together with the starting TiO_2 powder of ST-01. Here, abbreviations of 0, conv., SCW, mod. and rap. denote starting material, conventional under air atmosphere without water and NaCl, super-critical water, moderate and rapid temperature changes, respectively. The similarities of the XRD patterns suggested that the annealing treatments had no influence on the chemical composition of the TiO_2 powder.

Table 1 summarizes detailed annealing parameters and crystallite diameters calculated by the Scherrer's equation using the characteristic values of respective XRD peaks at around 25.3 degrees. Compared to the starting TiO_2 powder, larger crystallite diameters were always observed in the annealed TiO_2 powders regardless of the operating conditions. Among the annealed TiO_2 powders, the crystallite diameter annealed via the conventional technique was smaller than those obtained with the invented annealing techniques using critical water and/or NaCl [11] [12], meaning sufficient evidences for superiority of the invented critical water annealing processes.

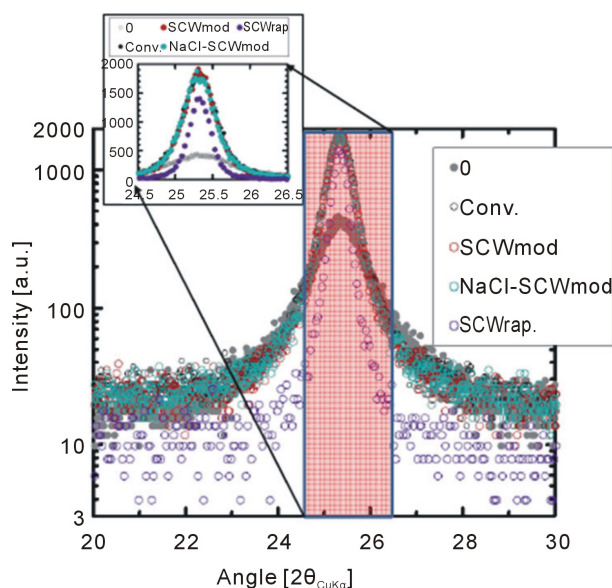


Figure 3. XRD patterns of TiO₂ powders.

Table 1. Crystallite diameters (*i.e.* Scherrer sizes) of TiO₂ powders.

0	Starting TiO ₂ Powder, ST-01		13.0 nm
Abbreviations	Annealing conditions		Crystallite diameter
	Heating rate	Quenching rate	
Conv.	6 K/min	Spontaneously	30.8 nm
SCWmod.	6 K/min	Spontaneously	47.2 nm
NaCl-SCWmod.	6 K/min	Spontaneously	50.3 nm
SCWrap.	Very rapid	Very rapid	33.4 nm

3.2. Crystallite Diameter Comparisons between TiO₂ and Pt/TiO₂ Powders

As described above, Pt loading treatments affected crystallite diameters of the (Pt-loaded) TiO₂ powders. **Table 2** shows all crystallite diameters of the Pt/TiO₂ powders together with those before Pt loading as already shown in **Table 1**. To find the effect of Pt loading treatments on the crystallite diameters of TiO₂ powders, **Figure 4** shows crystallite diameters of Pt/TiO₂ powders divided by those of the respective TiO₂ powders before Pt loading.

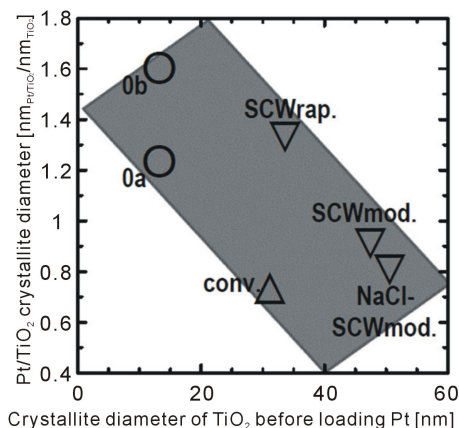
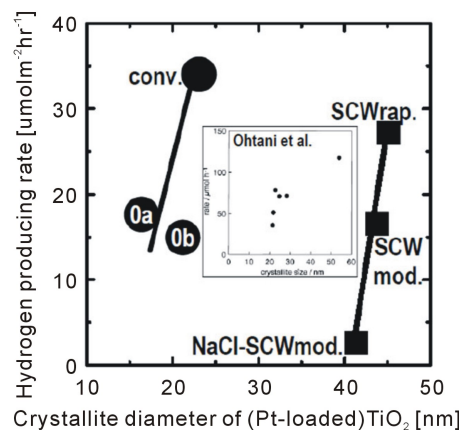
This figure roughly indicates inversely proportional relation in the crystallite diameters of TiO₂ and Pt/TiO₂ powders. Furthermore, it can be seen that difference of the crystallite diameters in Pt/TiO₂ powders prepared from the same TiO₂ powder is not a negligible quantity (see 0a and 0b in **Table 2** and **Figure 4**) on account of different experimenters. It is fairly common in photocatalytic reactions to obtain such inconsistent results, however the invented annealing processes are prodigious to give strong data repeatability for all inorganic powders [11]–[13]. Consequently, differing crystallite diameters of the (Pt-loaded)TiO₂ powders prepared from the same TiO₂ powder such as 0a and 0b could be attributed to fine procedural inconsistencies during Pt loading treatments such as the time duration of various steps, position of the black light affecting ultraviolet intensity to TiO₂ powder, and stirring intensity.

3.3. Water Splitting by Pt/TiO₂ Powders with Various Crystallite Diameters

Figure 5 shows hydrogen producing rates by photocatalytic water splitting with crystallite diameters of (Pt-loaded) TiO₂ powders ranging from 16 to 23 and from 41 to 45 nm together with superimposing a fruitful figure from a reference literature [10]. It can be seen that hydrogen producing rates were increased steeply towards the crystallite diameter of (Pt-loaded) TiO₂ powder in the above-mentioned two ranges. Quantitatively,

Table 2. Crystallite diameters of TiO₂ powders before and after loading Pt.

Abbreviations	Crystallite diameter [nm]	
	TiO ₂	Pt/TiO ₂
0a	13.0	16.2
0b	13.0	21.0
Conv.	30.8	22.9
SCWmod.	47.2	43.6
NaCl-SCWmod.	50.3	41.2
SCWrap.	33.4	44.9

**Figure 4.** XRD patterns of TiO₂ powders.**Figure 5.** XRD patterns of TiO₂ powders.

hydrogen producing rates were increased from around 15 and a little over 2 to about 30 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ with slight increments of the crystallite diameter of (Pt-loaded)TiO₂ powder in the order of a few nanometers for respective ranges.

Such steep increments resemble the results on the superimposed figure in **Figure 5** at around 20 nm of anatase TiO₂ crystallite sizes obtained by Ohtani and co-workers [10], approaching to a local maximum hydrogen producing rate of about 75 $\mu\text{mol}\cdot\text{hr}^{-1}$. However, it can also be seen that this rate has been unchanged for relatively wide range in about 10 nm of anatase TiO₂ crystallite sizes from about 20 to 30 nm, and then a champion rate about 120 $\mu\text{mol}\cdot\text{hr}^{-1}$ discretely reveals at around 55 nm of TiO₂ crystallite size [10].

Concerning relations among crystallite diameters, lattice defects (such as vacancies, impurities and dislocations) and band structures (such as highest occupied molecular orbital, lowest unoccupied molecular orbital and

their difference so-called a band-gap) of TiO₂ powders, the followings are commonly endorsed [17] [18]: lattice defects broaden a band-gap range, smaller crystallite diameters enlarge a band-gap itself so-called a blue-shift, crystallite diameter increments bring with decreases of any lattice defects, and so on. Hence, increasing crystallite diameters of anatase ST-01 powders may result in approaching 3.2 eV as pure anatase TiO₂ on a single crystal state a whole volume of each powder having broad band-gaps originally. This can elucidate the results in **Figure 5**, that is to say, ST-01 crystallite diameter increments lead to contradictive enhancing and descending effects on photocatalytic water splitting rates. Concretely describing, the rate enhancements have been due to increasing ST-01 volume playing photocatalytic water splitting role gradually in accordance with decreasing their lattice defects, while the rate descents have been owing to narrowing the band-gaps approaching to 3.2 eV, resulting to invalidation of the activating light intensity especially ranged from 380 to 400 nm. Such simultaneous effects of enhancing and descending photocatalytic water splitting rates due to increments of TiO₂ crystallite diameters are supposed to result in discontinuous hydrogen producing rates towards crystallite diameters of the (Pt-loaded) TiO₂ powders as shown in **Figure 5**.

In order to verify the above-mentioned mechanisms based on some assumptions, experiments with the (Pt-loaded)TiO₂ powders in crystallite diameters from 23 to 41 and above 45 nm are indispensable, however it is so difficult to prepare mid-crystallite-sized (from 40 to 50 nm) TiO₂ powders to borrow Ohtani and co-workers' phrases in their paper [10]. Anyway, the authors succeeded to prepare the mid-crystallite-sized TiO₂ powders of 41.17, 43.65 and 44.95 nm accurately. Furthermore, steep increments of hydrogen producing rates could be obtained with an increase in crystallite diameter of the (Pt-loaded)TiO₂ powder as described-above. On the grounds of these outcomes, much further higher photocatalytic water splitting rates can be expected with a bit change of the (Pt-loaded)TiO₂ crystallite diameter by using the invented novel annealing processes [11] [12].

4. Future Strategies for Enhancing Photocatalytic Water Splitting Rate

As mentioned above, this study expanded Scherrer size ranges of Pt/TiO₂ powders to some extent. However, the aforementioned blank regions from about 23 to 41 and above 45 nm remain to be studied. **Tables 3** shows parameters of interest of Pt/TiO₂ powders. In order to systematically study the relative effects of each parameter of interest on the resulting hydrogen production rate, the optimal Pt/TiO₂ powder and its respective annealing treatment and Pt loading must first be determined.

There are many commercially prepared TiO₂ powders as shown in **Table 4**. Previous works in literature point to P90, manufactured by Nippon Aerosil Co., Ltd., as the best commercially available photocatalyst for water splitting reactions [5]. Therefore, any further experimentation will utilize P90 (or any TiO₂ powder subsequently deemed superior) as the TiO₂ starting material.

Table 3. Considerable operating parameters for varying (Pt-loaded)TiO₂ crystallite diameters.

Annealing treatments		
Parameters	This study	Future
Temperature	660 K	Higher or lower
Heating rate	6.0 K/min or very rapid	Higher or lower
Pressure	26.1 MPa	Higher or lower
Powder/water ratio	1.0 g/3.0 mL	More or less
Holding time	1.0 hr	Longer or shorter
Salt	NaCl	Others
Pt loading treatments		
Parameters	This study	Future
Pt loaded	0.1 wt%	More or less
Light	15 W	Higher or lower
Stirring	1000 r.p.m.	Higher or lower
Drying temperature	373 K	Higher or lower
Drying duration	24 hr	Longer or shorter

Table 4. Examples of commercial TiO₂ and suitable applications confirmed by the authors so far.

Company	Name of TiO ₂	Suitable applications
Fuji Titanium Industry Co., Ltd.	“TA” series as TA-100	Unconfirmed
Ishihara Sangyo Kaisha, Ltd.	“ST” series as ST-01 utilized in this study	Beta plus for both water splitting [5] and purification [19]
Nippon Aerosil Co., Ltd.	“P” series as P25 and P90	Water splitting [4] [5]
Sachtleben Chemie GmbH	AN, SA and LO-CR-K	Unconfirmed
Tayca Co.	“MT” and “JA” series as MT-150A and JA-1	Unconfirmed
Titan Kogyo, Ltd.	“STT” series as STT-65C-S	Unconfirmed
Wako Pure Chemical Industries, Ltd.	Reagents	Water purification [19]-[21]

5. Conclusion

Due to the novel critical water annealing process, (Pt-loaded)TiO₂ powders with various crystallite diameters (*i.e.* Scherrer sizes) ranging from about 16 to 23 and 41 to 45 nm could be prepared. The photocatalytic hydrogen producing rate (water splitting rate) was enhanced from around 15 and a little over 2 to about 30 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ with slight increments in crystallite diameter from 16 to 23 and from 41 to 45 nm, respectively. Further water splitting rate enhancements were concluded possible through optimization of crystallite diameters of (Pt-loaded)TiO₂ and selection of an optimal TiO₂ powder as a starting material.

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