



High-temperature calcination and hydrogen reduction of rutile TiO₂: A method to improve the photocatalytic activity for water oxidation



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ABSTRACT

Rutile titania (TiO₂) is an efficient photocatalyst for oxidizing water to O₂. The photocatalytic activity of particulate rutile for water oxidation was significantly improved by H₂ reduction at 700 °C, after calcination at 1100 °C. The improved activity was due to an increase in crystalline size during calcination, and an increase in conduction band electron concentration by the creation of oxygen vacancies. In contrast to the consideration that oxygen vacancy increases the recombination of electron and holes, the hydrogenated TiO₂ exhibited high apparent quantum efficiency for O₂ evolution, 41% under irradiation at 365 nm. It was found that H₂ treatment improved the photocatalytic activity per unit of surface area not only for O₂ evolution but also for H₂ evolution and acetic acid decomposition. The effect of H₂ reduction treatment was obtained only if the rutile particle was previously calcined at temperatures higher than 1000 °C. This suggests that space charge layer in large crystalline particles is involved in the activation mechanism of hydrogenated rutile TiO₂ particles.

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1. Introduction

Solar water-splitting on oxide photocatalysts and semiconductor electrodes is attractive, because of its potential for H₂ production using renewable energy [1–5]. A significant enhancement of the photocatalytic activity for solar energy conversion to chemical fuels is necessary for practical use. However, the design concepts of optimized efficiency photocatalysts have not been clear, even for the typical n-type oxide photocatalyst TiO₂. Rutile TiO₂ particles reportedly achieved photocatalytic splitting of pure water into H₂ and O₂, but the quantum efficiency was estimated to be low, about 1% at 350 nm [6].

Decreasing the density of crystal defects is generally considered to increase the utilization of photoexcited electrons and holes. This is because defects act as recombination centers. Crystal defects in non-doped n-type TiO₂ are considered to be O vacancies and Ti³⁺. Strong oxidation at elevated temperatures can reportedly decrease the density of defects in TiO₂ [7,8]. Therefore, high-temperature annealing in air is likely to improve the photocatalytic activity.

O vacancies form also shallow donor states below conduction band originating from Ti 3d orbitals, which can even overlap the conduction band in the case of highly deficient TiO₂ [9]. The increase of the concentration of electrons enhance the electrical

conductivity of TiO₂ [7]. Actually, single crystal rutile electrodes are often treated by H₂ reduction, to generate O vacancies and improve their electrical conductivity and photoelectrochemical efficiency [10–12].

H₂ reduction treatment has received much recent attention, for improving the photoactivity of anatase TiO₂ nanostructures [13–18]. It works by creating defect disorders on the surface. However, the O vacancy of anatase TiO₂ is considered to be unstable in air even at room temperature, and the enhanced photocatalytic activities of hydrogenated TiO₂ are open for discussion [19,20]. Most investigations have focused on hydrogenated anatase rather than rutile TiO₂. There are few reports on H₂ reduction treatment on particulate rutile photocatalysts, despite rutile being an important photocatalyst for water splitting.

We recently reported that high-temperature calcination deactivated the photocatalytic activity of rutile TiO₂ particles with small specific surface area (2.3 m² g⁻¹). Subsequent H₂ reduction treatment then improved the activity of the same sample [21]. The surface area was constant during calcination, so deactivation was not attributed to specific surface area changes. Deactivation was partly attributed to a decrease in long-lived photoexcited carriers, accompanied with a decrease in O vacancies through the high-temperature calcination.

Crystalline size is another factor affecting the lifetime of photogenerated charge carriers in photocatalysts. In the photocatalytic O₂ evolution by water oxidation, anatase particles exhibit poor activity, while larger rutile particles are more efficient

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[22–24]. Large tungsten trioxide (WO₃) particles with low surface area-to-volume ratios are well-suited to providing long-lived photogenerated holes. This is because slow bulk recombination is the dominant process in larger particles, rather than fast surface recombination [25].

Controlling the crystalline size and O vacancy density is expected to improve the activity of particulate photocatalysts, for O₂ evolution by water splitting. In the current study, we investigated the effect of crystal growth and defect density on the photocatalytic activity of large specific surface area (17 m² g⁻¹) rutile particles. High-temperature calcination and H₂ reduction effectively improved the surface reactivity of rutile photocatalysts. We have found that the effect of H₂ reduction is obtained only for rutile particles with large crystalline size after high temperature calcination.

2. Experimental

2.1. Materials

High purity TiO₂ powder, F-1R (0.02 wt.% Cl), was sourced from Showa Titanium (Toyama, Japan). The powder in an alumina crucible was calcined at 300–1250 °C for 2 h in air, using an electric furnace. After calcination at high temperature, the sample was lightly ground in an alumina mortar. H₂ reduction of the rutile powder was performed in a quartz tube reactor under atmospheric pressure. The sample in a quartz boat was placed in the reactor. The temperature was increased to 700 °C, under a stream of 50 mL min⁻¹ H₂. After 2 h under the H₂ flow, the sample was cooled to 300 °C under H₂ flow, and then to room temperature under N₂ flow. The sample name Fx00–H700 indicates that F-1R was calcined at x00 °C, followed by H₂ reduction at 700 °C.

2.2. Photocatalytic activity tests

Photocatalytic activity was examined using three test reactions: (A) O₂ evolution with the deposition of Ag⁰ on the photocatalyst surface, from aqueous 50 mmol L⁻¹ AgNO₃ (>99.8%, Wako Pure Chemical Industries, Osaka, Japan) under Ar; (B) H₂ evolution from aqueous 50 vol.% ethanol with hexachloroplatinic acid (H₂[PtCl₆]·6H₂O, >98.5%, Kanto Chemical, Tokyo, Japan) for in situ Pt deposition (2.0 wt.%); (C) oxidative decomposition of 1.0 vol.% aqueous acetic acid under O₂. The 50 mg TiO₂ powder suspension in 9.0 mL of solution in a glass tube with an outside diameter of 18 mm was magnetically stirred, and irradiated by UV emitting diodes (LEDs) at room temperature. The LED wavelength was centered at 380 nm, with a half width of 12 nm. The irradiance was measured to be about 10 mW cm⁻². The amount of evolved gas was quantified by gas chromatography, with a Molecular Sieve-5A column and Porapak-Q column.

Quantum efficiency was measured using monochromatic light through a bandpass filter (central wavelength 365 nm, half bandwidth 10 nm) emitted from a 300 W Xe lamp (ILC Technology CERMAX-LX300). The intensity of irradiation was measured by an optical power meter (Hioki 3664). The apparent (or external) quantum efficiency (AQY) was calculated as the ratio of the rate of electron consumption, assuming that O₂ evolution is a 4e⁻ process, to the flux of incident photons (~1.7 × 10⁻⁶ einsteins min⁻¹).

2.3. Characterization

Scanning electron microscopy (SEM) images were recorded using a Hitachi S-5200 instrument. Specific surface areas were determined using Brunauer–Emmett–Teller (BET) plots from N₂ absorption isotherms at -196 °C, measured with a Bel Japan BELSORP-mini instrument. X-ray diffraction (XRD) patterns were

recorded on a Rigaku RINT-2000/PC diffractometer, with Cu Kα radiation. Nickel oxide was used as an internal standard. The weight fraction of rutile phase in the anatase-rutile mixture (X_R) was estimated from:

$$X_R = \frac{1.26I_R}{(I_A + 1.26I_R)}$$

where I_R and I_A are the intensities of the rutile(110) and anatase(101) peaks, respectively [26]. The diameter of rutile crystalline domains was estimated from the half width of rutile(110) peaks, using the Scherrer equation. Diffuse reflectance ultraviolet–visible–near infrared (UV–Vis–NIR) spectra were obtained using an ALS SEC2000 spectrometer, with a Hamamatsu Photonics L10290 fiber light source and barium sulfate reference.

3. Results

3.1. Characterization of rutile TiO₂ particles

Commercial TiO₂ (F-1R, Showa Titanium) was used as a photocatalyst. Fig. 1 shows SEM images of F-1R and samples calcined at different temperatures for 2 h. Samples calcined at x00 °C are denoted as Fx00. The particle size gradually increased with increasing calcination temperature. After calcination at 1100 °C, the particle size had increased to ~1 μm. This crystal growth caused the specific surface area of F-1R (17 m² g⁻¹) to consistently decrease, with increasing calcination temperatures at >700 °C as shown in Fig. 2. The specific surface area of F1100 was 1.6 m² g⁻¹.

XRD patterns indicate that F-1R possessed a rutile TiO₂ phase, with a small fraction of anatase (Fig. A.1 in Appendix A. Supplementary data). The weight fraction of rutile F-1R was ~96%. XRD peaks assigned to anatase disappeared after calcination at 900 °C. The diameter of crystalline domains was estimated by the Scherrer equation, and consistently increased with increasing calcination temperature at >700 °C (Fig. A.2). The crystal growth resulted in an increased particle size and decreased specific surface area.

Fig. 3 shows diffuse reflectance UV–Vis–NIR spectra. The photoabsorption edges due to transition from the valence to conduction bands occurred at approximately 420 nm. This corresponded to the 2.95 eV band gap of rutile TiO₂. There was a difference in the baseline intensity at 420–1050 nm in the spectra. The NIR intensity gradually decreased with increasing calcination temperature. The broad NIR absorption was assigned to the excitation of conduction band electrons, and therefore reflected the carrier concentration in the conduction band [27]. The decrease in intensity upon high-temperature calcination suggested a decreased conduction band electron concentration with crystal growth. This might be related to the decrease of defects upon high-temperature calcination. Strong oxidation reportedly facilitates the transformation of O-deficient to stoichiometric TiO₂ and then metal-deficient TiO₂, with p-type properties [7,8].

3.2. Hydrogen reduction of rutile TiO₂

H₂ reduction treatment of the calcined samples was then carried out. Hydrogenation creates surface O vacancies, and is accompanied by the formation of Ti³⁺ species according to Scheme 1. The optimum H₂ reduction temperature was 700 °C. Samples treated with H₂ at 700 °C for 2 h are denoted as Fx00–H700. F1100–H700 was a pale blue color, which remained stable in air at room temperature for in excess of one year. The diffuse reflectance spectra show an intense UV absorption assigned to interband transition, and a broad visible–NIR absorption (Fig. 3). The blue coloration and broad visible–NIR absorption were explained by the presence of conduction electrons associated with the generation of O vacancies and Ti³⁺ species [27]. The intensity of the broad visible–NIR absorption

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