# Enhanced Photocatalytic Activity by Particle Morphology—Preparation, Characterization and Photocatalytic Activities of Octahedral Anatase Titania Particles

Zhishun Wei,[1] Ewa Kowalska,*[1,2] and Bunsho Ohtani[1,2]
[1]*Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan*
[2]*Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan*

(Received <Month> <Date>, <Year>; CL-<No>; E-mail: kowalska@cat.hokudai.ac.jp)

Titania samples containing octahedral anatase particles (OAPs) were prepared by the ultrasonication–hydrothermal process of partially proton-exchanged potassium titanate nanowires. It was found that increase in ultrasonication time changed the morphology of products with other structural properties such as specific surface area, crystalline size and crystallinity remaining almost constant. Results of photocatalytic activity tests for those samples suggested higher activity of a sample with higher OAP content, especially for reaction in the presence of oxygen.

Titanium(IV) oxide (titania) has been used extensively for many years as a photocatalyst, mainly owing to its redox ability, stability and nontoxicity.[1-2] Though hundreds of papers on titania photocatalysis have been published, the essence of its photocatalytic activity, e.g., the reason of various levels of photocatalytic activity of samples with various properties and polymorphic composition, has not been clarified.[3] Recently, morphology of crystallites, widely studied for reactions occurring on a titania single crystal (mainly rutile (110))[4] but having been neglected for particulate photocatalysts, has been considered as one of the crucial factors of photocatalytic activity of particulate titania on the basis of the results of studies using facetted octahedral[5-7] and decahedral[8-10] anatase particles. We have recently developed an ultrasonication (US)–hydrothermal reaction (HT) process[11] to prepare octahedral anatase particles (OAPs), exposing eight equivalent {101} facets that are themodynamically the most stable, with enhanced photocatalytic activity, especially for oxidation of acetic acid in aerated aqueous solutions, compared with many commercial titania samples with similar properties. However, proof of higher activity only owing to OAP morphology has not yet been obtained, since particles with the same structural properties except for morphology could not be prepared. In order to prove the effect of particle morphology on photocatalytic activity, we examined various preparation conditions. In this paper, we represent the results for preparation of samples with different OAP contents and with other structural properties remaining almost constant and we show a comparison of their photocatalytic activities.

Samples were fabricated by the US–HT process (for details, see SI) using partially proton-exchanged potassium-titanate nanowires (TNW; Earthclean Tohoku Co. Ltd.) prepared by HT reaction of Evonik P25 (Nippon Aerosil) in a potassium hydroxide solution (17 mol $L^{-1}$) at 383 K for 20 h followed by washing with dilute hydrochloric acid.[12] Controlled parameters were US time (0–4 h), HT reaction time (3–48 h) and HT temperature (413–473 K). The products were collected by centrifugation and vacuum drying (353 K, 12 h).

Specific surface area of the products was estimated by nitrogen adsorption at 77 K using the Brunauer-Emmett-Teller (BET) equation. Crystallinity (anatase content) as well as crystallite size and morphology were measured by X-ray diffractometry (XRD; Rigaku SmartLab) and scanning electron microscopy (SEM; JEOL JSM-7400F), respectively. Particles in a sample were classified into three groups based on results of SEM analysis as shown in Fig. 1: (a) OAP: an octahedral particle without observable defects, (b) semi-OAP: an octahedral particle with a defect (defects) and (c) others: an irregular shaped non-octahedral particle. Composition of these particles in each sample was measured by counting at least 200 particles in several SEM images of a sample. The chemical formula and atomic composition of TNW and the products were examined by thermogravimetry (TG; ULVAC-RIKO TGD-9700), X-ray photoelectron spectroscopy (XPS; JEOL JPC-9010MC) and SEM with energy dispersive X-ray spectroscopy (SEM/EDS, JEOL JSM-6360LA).

An XRD pattern of TNW resembled a pattern of potassium titanate $K_2Ti_8O_{17}$, and the composition was estimated to be $H_{1.32}K_{0.68}Ti_8O_{17}\cdot 4H_2O$ (see SI). Based on SEM observation, it was found that the wire structure of TNW remained in the product after the US–HT process (see SI), and thus the composition of the final product, a mixture of hydrated titania with partially proton-exchanged potassium titanate, was estimated to be, e.g., $TiO_2\cdot 0.026(H_{0.83}K_{1.17}Ti_8O_{17})\cdot 0.24H_2O$ for the sample prepared by 1-h US and 6-h HT at 433 K. As expected, water content and molar ratio of remaining TNW decreased with increases in HT time and temperature. Thus, the US-HT process produced anatase crystallites with a small amount of titanate.

Influence of HT time on structure of the products was examined with other parameters kept constant, i.e., 1-h US and 433-K HT temperature, as shown in Fig. 2. With increase in HT time, titanate wires were converted into anatase crystallites, resulting in crystallinity increase, and specific surface area, water content and K/Ti (data not shown) were decreased, while HT time longer than 9 h did not change the structural properties. This indicates that most of the TNW

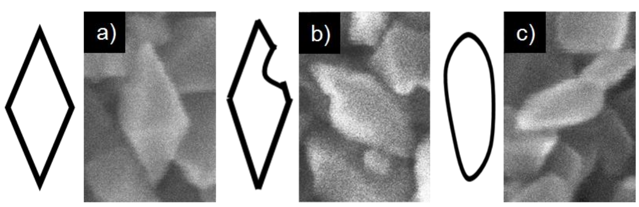


**Fig. 1** Representative SEM images of a) OAP, b) semi-OAP and c) others.

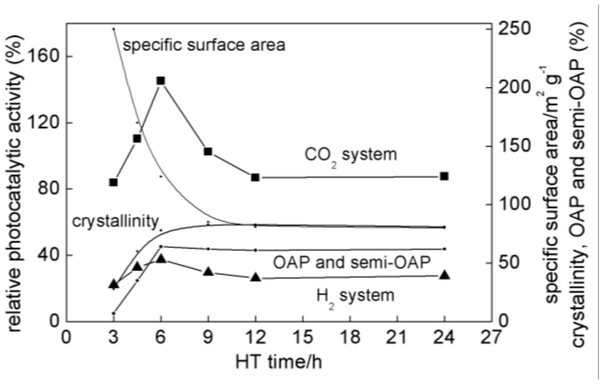


**Fig. 2** Crystallinity, specific surface area and photocatalytic activities as a function of HT time (433-K HT temperature and 1-h US).

was converted into anatase crystallites at > 9 h. Microscopic observations confirmed the presence of TNW for a short HT time (3 h) and almost complete disappearance of TNW for a longer reaction time.

HT time-dependent photocatalytic activities in the systems (for details, see SI) of mineralization of acetic acid in an aerated aqueous solution ($CO_2$ system) and dehydrogenation of methanol in a deaerated aqueous solution with an in-situ platinized (2wt%) photocatalyst ($H_2$ system) are also shown in Fig. 2. Although the photocatalytic activity in the $H_2$ system relative to that of the standard (FP-6) was low (< 40%), being consistent with our previous results,[11] its HT time-dependence was similar to that in the $CO_2$ system, which was higher than that of the standard. The activities reached maximum values (ca. 40% and 150% for $H_2$ and $CO_2$ systems, respectively) at 6-h HT time. In the conventional understanding, balance between high crystallinity and sufficient specific surface area might be responsible for the highest photocatalytic activity. It has been reported that sufficient specific surface area resulting in a large amount of adsorbents increases the rate of capture of electrons and positive holes by them, while high crystallinity induces a smaller amount of defects and thus reduces recombination of electrons and positive holes, resulting in enhancement of the photocatalytic activity.[13] However, it should be noted that the sample with the highest level of photocatalytic activity also possesses the highest content of OAP and semi-OAP, as shown in Fig. 2. Thus, the dependence of photocatalytic activity on structural properties seems to be complex, and the trend could not be interpreted only by crystallinity or specific surface area.

The influence of HT temperature on structural properties and thus on photocatalytic activity was also investigated with US time and HT time kept at 1 h and 6 h, respectively. The data obtained (not shown) are similar to the results for the above-mentioned influence of HT time, i.e., at a lower temperature (413 K), the presence of TNW was observed, and an increase in HT temperature above 433 K (similar to the increase in HT time) resulted in their disappearance. With an increase in HT temperature, specific surface area, water content and K/Ti of the products decreased, while crystallinity increased. As a result, HT temperature influenced photocatalytic activities in the $CO_2$ and $H_2$ systems. The photocatalytic activity in the $H_2$ system was less sensitive to HT temperature than was that in the $CO_2$ system. The optimum photocatalytic activities in the $CO_2$ system reached 150% for the sample prepared at 433 K. The dependence of photocatalytic activity on the properties could also not be interpreted by crystallinity or specific surface area alone, and it could be concluded that the balance between them resulted in the higher photocatalytic activity.[13] This hypothesis is supported by observation that the highest content of OAP and semi-OAP (66%), for the sample prepared at 453 K, correlated with the highest crystallinity (88%) but not with the highest level of photocatalytic activity (at 433 K), and thus not OAP content but balance between crystallinity and specific surface area could be crucial. This conclusion contradicts the previous one, for the influence of HT time, showing that morphology can be responsible for photocatalytic activity. However, as has already been mentioned, to find the real dependence and key factor of photocatalytic activity, a clear relation between only two parameters should be drawn.

As has been shown before, change in the preparation conditions of samples (HT time and temperature) caused change in their photocatalytic activity, morphology, and structural properties (specific surface area, crystallinity and crystallite size). In order to study the correlation between OAP morphology and photocatalytic activity, the structural properties should be kept the same (at least almost constant). It has been found that control of US time results in production of such samples possessing almost the same structural properties and different OAP contents.

US influenced the morphology of the precursor TNW; the length of TNW was shortened by 1-h US (a standard condition) as shown in Fig. 3, indicating that US could also influence the morphology of the final product. Indeed, the

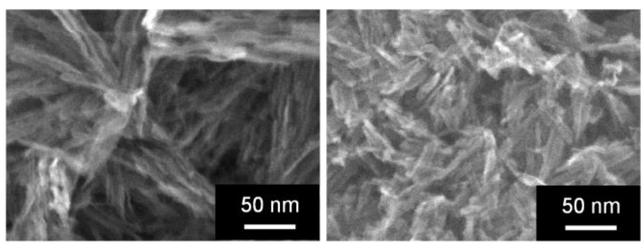


**Fig. 3** SEM images of TNW before (left) and after 1-h US (right).

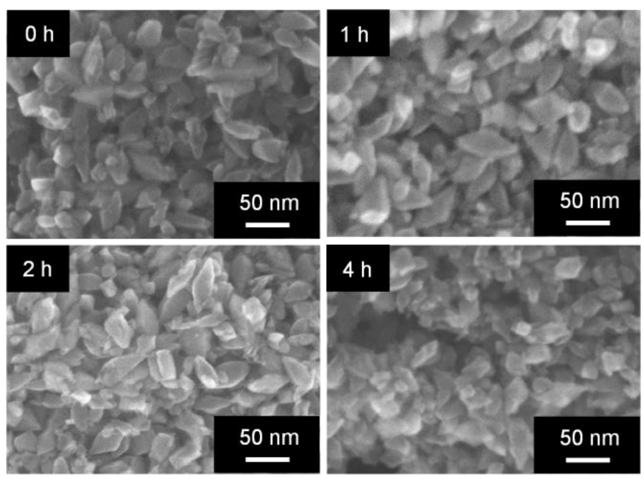


**Fig. 4** SEM images of samples prepared with various US times (0 h, 1 h, 2 h and 4 h).

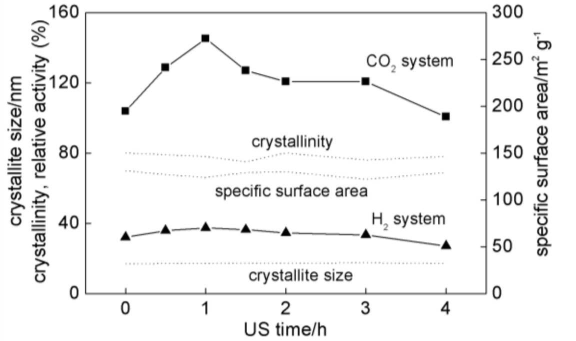


**Fig. 5** Correlations between crystallinity, specific surface area and photocatalytic activity for OAPs prepared by 6-h HT at 433 K.

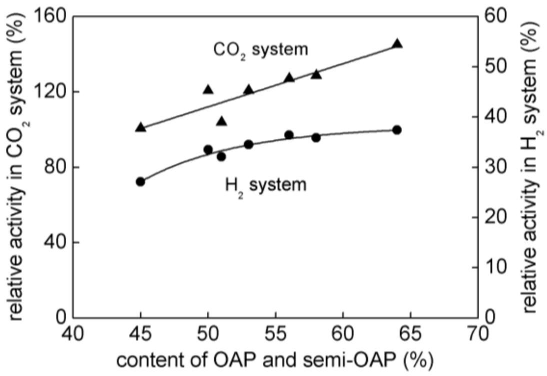


**Fig. 6** Correlation between photocatalytic activity and content of OAP and semi-OAP.

morphology of final products depended on US time (Fig. 4), and the content of OAP and semi-OAP was 51%, 64%, 53% and 45% for 0, 1, 2 and 4-h US, respectively (detailed data are shown in Table S1 and Fig. S3 of SI). However, the structural properties (crystallinity, specific surface area, crystallite size and water content) of these products were almost the same, as shown in Fig. 5. It was clearly observed that the photocatalytic activities differed for samples with almost the same structural properties (Fig. 5), which may exclude the possibility that the balance between specific surface area and crystallinity accounts for a high level of photocatalytic activity.

The correlation between photocatalytic activities in $H_2$ and $CO_2$ systems and content of OAP and semi-OAP is shown in Fig. 6. The photocatalytic activity, especially in the $CO_2$ system, increased with an increase in OAP and semi-OAP content, suggesting that the photocatalytic activity is governed mainly by the morphology; photocatalytic activity of OAP (and semi-OAP) is higher than that of the others. Based on the assumption, as the first-step approximation, that OAP and semi-OAP have equal activity and the overall activity is a weighted average of activities of OAP and the others, the linear line for the $CO_2$ system suggests that photocatalytic activities of pure OAP and the others are formally ca. 230% and almost 0% (as relative activity), respectively, i.e., more than twice higher activity could be obtained if pure OAP is prepared. Thus, this rough estimation suggested the negligible activity of the others, though those particles may show appreciable but relatively low-level of activity. Since the trends in variation of OAP and semi-OAP contents depending on the US-time were similar (see Fig. S3 in SI), discrimination of photocatalytic activity of OAP, semi-OAP and the others seems difficult without isolation of three kinds of particles, which is the next challenge.

Then, why does OAP show higher activity? One possible explanation is that OAP has preferred crystal lattice defects, which can be evaluated as electron traps working as a recombination center and a surface-adsorption site. Preliminary results of measurement of such electron traps (ETs) by double-beam photoacoustic spectroscopy[14] showed that total ET density of the samples prepared with different US times was almost constant. It is expected that shallow and deep ETs in the band gap enhance the migration of electrons and recombination, respectively, and thereby even if total ET density is the same, distribution of differences in the depth of ET may regulate the photocatalytic activity. Study on energy-resolved measurement of ETs for the present samples is now under way.

The reason for the low level of photocatalytic activity in the $H_2$ system is still unknown. It should be noted that the $H_2$ system requires noble-metal deposition, and it has been reported that reductive deposition as in the case of in-situ platinum deposition of a noble metal occurred preferentially on {101} facets.[8,15] Further studies on mechanisms of specified redox reactions on OAPs are presently under way.

In conclusion, samples of almost the same structural properties with various OAP (and semi-OAP) contents have been successfully prepared through the US–HT process with various US times and constant HT time and temperature. Photocatalytic activities of these samples suggested that OAP morphology enhanced the activity, especially for the photocatalytic reactions involving oxygen uptake.

## Acknowledgement

One of the authors (ZW) appreciates China Scholarship Council (CSC) for support.

## References

1 M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69.
2 A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.* **2008**, *63*,515.
3 For example: O.-O. Prieto-Mahaney, N. Murakami, R. Abe, B. Ohtani, *Chem. Lett.* **2009**, *38*, 238.
4 For example: M. Li, W. Hebenstreit, U. Diebold, A. M. Tyryshkin, M. K. Bowman, G. G. Dunham, M. A. Henderson, *J. Phys. Chem. B* **2000**, *104*, 4944.
5 M. Miyauchi, *J. Mater. Chem.* **2008**, *18*, 1858.
6 N. Murakami, Y. Kurihara, T. Tsubota, T. Ohno, *J. Phys. Chem. C* **2009**, *113*, 3062.
7 B. Ohtani, F. Amano, T. Yasumoto, O.-O. Prieto-Mahaney, S. Uchida, T. Shibayama, Y. Terada, *Top. Catal.* **2010**, *53*, 455.
8 T. Ohno, K. Sarukawa, M. Matsumura, *New J. Chem.* **2002**, *26*, 1167.
9 H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Naure*, **2008**, 453, 638.
10 F. Amano, O.-O. Prieto-Mahaney, Y. Terada, T. Yasumoto, T. Shibayama, B. Ohtani, *Chem. Mater.*, **2009,** 21, 2601.
11 F. Amano, T. Yasumoto, O.-O. Prieto-Mahaney, S. Uchida, B. Ohtani, *Chem. Commun.* **2009**, 2311.
12 S. Uchida, Y. Sanehira, Jpn. Pat., P2005-162584A, **2005**.
13 H. Kominami, T. Matsuura, K. Iwai, B. Ohtani, S. Nishimoto, Y. Kera, *Chem. Lett.* **1995**, 693.
14 N. Murakami, O.-O. Prieto-Mahaney, R. Abe, T. Torimoto, B. Ohtani, *J. Phys. Chem. C* **2007** *111*, 11927
15 C. Liu, X. Han, S. Xie, Q. Kuang, X. Wang, M. Jin, Z. Xie, L. Zheng, *Chem. Asian J.* **2013**, *8*, 282.
16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

NOTE *The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge.*
*For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF.*
*If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.*

# Graphical Abstract

## Textual Information

| | |
|---|---|
| Description (if any) | Effect of octahedral morphology to enhance photocatalytic activity was suggested by the activities of samples of almost the same structural properties with different octahedral particle contents. |
| Title | Enhanced Photocatalytic Activity by Particle Morphology—Preparation, Characterization and Photocatalytic Activities of Octahedral Anatase Titania Particles |
| Authors' Names | Zhishun Wei, Ewa Kowalska and Bunsho Ohtani |

## Graphical Information