The mechanism of formation of hierarchical "flake-ball"-structured bismuth tungstate (BTO) particles was studied on the basis of structural analyses and was revealed to be growth of plate-like BTO crystallites on the tungsten oxide/BTO-modified surface of bismuth hydroxide particles by supplying tungsten and bismuth from the outside and inside of the core particles, respectively.
Mechanism of the Formation of Hierarchical-structured Bismuth Tungstate Photocatalyst Particles through Counter-flow Supply of Bismuth and Tungsten Sources

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The mechanism of formation of hierarchical “flake-ball”-structured bismuth tungstate (BTO) particles was studied on the basis of structural analyses and was revealed to be the growth of plate-like BTO crystallites on the tungsten oxide/BTO-modified surface of bismuth hydroxide particles by supplying tungsten and bismuth from the outside and inside of the core particles, respectively.

Heterogeneous photocatalysis is a key technology that has been applied and will continue to be applied to the conversion of solar energy into fuels1-10 and to the decomposition of environmental contaminants.3,4 Unfortunately, however, it should be recognized that there have been no guiding principles for the design of a highly active particulate photocatalyst based on the causal relation between structural/physical properties and photocatalytic activities of a photocatalyst.5 In other words, only empirical guidelines such as higher specific surface area and/or higher crystallinity have been believed to be necessary.6 Particle morphology also seems to be one of those guidelines; it has been reported in many papers7,8 that nano- or microstructured particles show higher photocatalytic activities than those of particles without morphological features. Taking into account that those characteristic morphologies originate in the crystal structure of a material, particles having characteristic morphology can be highly crystallized and thereby possess fewer crystal defects, reducing the probability of photoexcited electron-positive hole recombination.

One of the examples of such highly crystallized photocatalyst particles is “flake ball (FB)"-shaped bismuth tungstate (Bi2WO6; BTO) prepared by a hydrothermal (HT) reaction;9-12 an FB-BTO particle is a spherical micrometer-scale assembly of flakes of nanometer-scale plate-like BTO crystal layers, as shown in Figure 1. It has been claimed that such a hierarchical structure enables the crystallization of BTO by high-temperature calcination without lowering the specific surface area, since little sintering of BTO flakes is expected even when calcined at a high temperature. This may be a significant merit of the hierarchical FB morphology, and FB particles of a material other than BTO are therefore expected to have a high level of photocatalytic activity. In order to extend the morphology control to other materials, an attempt was made to clarify the mechanism of FB-BTO formation13-16 and the detailed structure and properties of FB-BTO particles. Although it was suggested in a previous paper12 that the mechanism of FB-BTO formation is not the assembly of BTO flakes liberated independently but anisotropic crystal growth on small BTO particles as a seed, further discussion is needed to fully understand the mechanism and real structure of FB-BTO.

FB-BTO particles were prepared by the HT reaction of a mixture of bismuth nitrate (Bi(NO3)3, 5.0 mmol) and sodium tungstate (Na2WO4, 2.75 mmol) in water (70 mL) at 433 K for 20 h according to a previous work.9 As has already been reported, FB-BTO particles, i.e., spherical assemblies of flakes with outer diameters of ca. 3-5 µm (Figure 1), were mainly produced (ca. 70-80% in number) under the conditions of 10% excess feeding of a tungsten source (Na2WO4), as described above with high reproducibility. This suggests that at least excess tungsten components must be in a non-crystalline phase. Based on the assumption that all of the bismuth is included as BTO and that excess tungsten forms tungsten oxide, the weight fraction of the latter, WO3, was calculated to be ca. 6%. The weight fraction of the non-crystalline component was estimated by Rietveld analysis of a mixture of a sample with a crystalline internal standard (nickel oxide; NiO, 20 wt %) (see Supporting Information (SI)) to be ca. 20% (the remaining ca. 80% was crystalline BTO). Taking the water content (ca. 1%), estimated by thermogravimetry (see SI), into account, the calculated amorphous component (ca. 19%) was much larger than the weight fraction of the above-mentioned excess tungsten component as WO3, suggesting that there must be an amorphous phase containing both bismuth and tungsten. Calcination of the as-prepared FB-BTO at 773 K for 3 h in air induced negligible further crystallization, i.e., the non-crystalline fraction in the calcined sample was still ca. 19%, and no appearance of non-BTO phases in the XRD pattern was observed, indicating that the amorphous tungsten-bismuth oxide component might be dispersed in the FB particles. Thus, an excess of the tungsten source (Na2WO4) must be a key factor for the production of FB-BTO particles.

Figure 2a shows the results of sonication in an acidic suspension of once-prepared FB-BTO particles. While a slight change, i.e., separation of flakes to crystalline plates, maintaining the outer particle size, was observed by sonication for 30 min (Figure 2d), prolonged sonication for >60 min decomposed the
FB structure (Figures 2e and 2f), and, surprisingly, there seemed to be vacancies in the particles. Although similar vacancies were seen for samples sonicated in water or an alkaline suspension (Figures 2b and 2c), in which tungsten oxide (WO$_3$) is expected to be dissolved, the observation of vacancies in the acidic suspension in which WO$_3$ is stable indicated that the vacancies in FB particles should be there before the sonication, i.e., the hollow structure was prepared during the HT synthesis. Preliminary experiments of cross-sectional SEM observation of FB-BTO by focused ion-beam milling also indicated the presence of a void space in an FB particle (data not shown). Another observation supporting the presence of a void space in an FB particle was the absence of solid core-like particles, which are expected for particles without void spaces, when FB particles were wet-milled; only crashed platelets could be seen in the SEM images (see SI). The observed high bulk specific volume (apparent specific volume including void spaces in and between the particles), >4 times larger than that of non-FB BTO prepared by solid state reaction (see SI), is attributable to this hollow FB structure.

Since it is unlikely that the FB particle-formation process is initiated by the assembly of BTO plates and/or flakes leaving spherical vacancies inside, the hollow spaces can be reasonably accounted for by dissolution/consumption of substantial spherical cores during the HT reaction using Bi(NO$_3$)$_3$ and Na$_2$WO$_4$ as sources of BTO. The most probable candidate of this core is bismuth hydroxide (Bi(OH)$_3$) liberated by rapid hydrolysis of once-dissolved Bi(NO$_3$)$_3$ in water to give a white suspension, as

$$\text{Bi(NO}_3\text{)}_3 + 3\text{H}_2\text{O} \rightarrow \text{Bi(OH)}_3 + 3\text{HNO}_3$$

(1)

In the process of FB-BTO preparation, an aqueous Na$_2$WO$_4$ solution was added dropwise to this acidic suspension, and a part of the nitric acid (total 15 mmol) might be neutralized by sodium hydroxide (maximally 5.5 mmol) released by the hydrolysis of Na$_2$WO$_4$ as,

$$\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{WO}_4 + 2\text{NaOH}$$

(2)

As a result, pH of the reaction mixture before HT treatment was strongly acidic (pH ca. 1.2), and this pH value was not changed by the HT treatment. It has been shown that, even without HT treatment, H$_2$WO$_4$ in an acidic medium is slowly polymerized (oligomerized) to be a gel, and formation of WO$_3$ particles may therefore proceed slowly when the reaction mixture contains only H$_2$WO$_4$. In the actual reaction mixture containing both Bi(OH)$_3$ and H$_2$WO$_4$, both Ostwald ripening of Bi(OH)$_3$ particles and BTO formation are expected to proceed in parallel based on the assumption that formation of WO$_3$ particles is slower than other reactions. The former process may produce thermodynamically stable spherical Bi(OH)$_3$ particles with monodispersed particle sizes, and the latter process occurs at the interface between Bi(OH)$_3$ particles (bismuth source) and an aqueous phase containing H$_2$WO$_4$ (tungsten source). One hypothesis is that a WO$_3$ or BTO layer is formed on the surface of Bi(OH)$_3$ in the middle stage of the HT reaction (after formation of monodispersed Bi(OH)$_3$ particles) and BTO crystal plates grow on the outer surface of the layer. Assuming that a tungsten source, oligomeric H$_2$WO$_4$, is less mobile and cannot penetrate the layer, tungsten is provided only from the outside, while bismuth is provided from the inside of particles through the layer, reducing the size of the Bi(OH)$_3$ core to produce a void space inside.

A control experiment was performed to prove the production of Bi(OH)$_3$ core particles; a Bi(OH)$_3$ suspension with sodium hydroxide with the molar amount identical to that of Na$_2$WO$_4$ was HT treated under the conditions same as those for FB-BTO preparation (see SI). SEM observation of the resultant product revealed the growth of non-spherical Bi(OH)$_3$ particles and their aggregation in the size of several tens micrometers. Although the size of those particles were larger than that expected from the FB-BTO particles according to the proposed mechanism, it is reasonable assuming that a tungsten component, H$_2$WO$_4$, may prohibit excess growth of Bi(OH)$_3$ under HT conditions by being deposited on the Bi(OH)$_3$ surface as BTO or WO$_3$. On the basis of these considerations, the proposed mechanism of FB-BTO production is shown schematically in Figure 3: (1) Ostwald ripening of Bi(OH)$_3$ particles, (2) deposition of a WO$_3$/BTO thin layer, and (3) growth of BTO crystalline plates (flakes) on the layer consuming Bi(OH)$_3$ to leave a void space inside.

Through this mechanism, the size of the final product, i.e., outer diameter, would be controlled essentially by the size of

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**Figure 2.** SEM images of FB-BTO after 90-min sonication in (a) acidic, (b) neutral (water) and (c) basic suspensions and time course of sonication for (d) 30, (e) 60, and (f) 90 min in the neutral suspension.

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**Figure 3.** Scheme of FB-BTO production mechanism.
core Bi(OH)$_3$ particles in the (early stage of) HT treatment as well as thickness (length) of BTO flake layers. As has been reported previously, the size of FB-BTO particles, as well as the thickness of flake layers, seemed to be slightly increased by the elevation of the HT temperature, resulting in a possible higher density of particles and thereby a decrease in the total number of particles (not assuming the inside void space). This is attributable to a possible larger Bi(OH)$_3$ particle size and a smaller number of particles at a higher HT temperature. In order to clarify the reason for the necessity of an excess tungsten source based on the above-described mechanism, control experiments with different W/Bi ratios and pH values were performed, and SEM images of the resultant products are shown in Figure 4 (see SI for details): (a) 5.0 mmol Bi(NO$_3$)$_3$ and 2.5 mmol Na$_2$WO$_4$ (W/Bi = 0.50), (b) 5.0 mmol Bi(NO$_3$)$_3$ and 2.75 mmol Na$_2$WO$_4$ (W/Bi = 0.55) with 0.50 mmol nitric acid, and (c) 5.0 mmol Bi(NO$_3$)$_3$ and 2.5 mmol Na$_2$WO$_4$ (W/Bi = 0.50) with 0.50 mmol sodium hydroxide. The stoichiometric W/Bi ratio condition (condition (a)) induced the production of smaller and non-uniform sized FB particles with a large fraction (73%) of non-FB particles, as has been reported previously, suggesting that the lower H$_2$WO$_4$ concentration and/or lower pH due to a lower concentration of sodium hydroxide in reaction (2) induces such changes in the product. Interestingly, similar products (65% non-FB particles) were obtained under condition (b), excess tungsten with lower pH, and therefore slightly lower pH than that of the standard conditions (though only a small decrease in pH was actually observed), but not a lower W/Bi ratio, may lead to a lower yield of uniform spherical Bi(OH)$_3$ particles to result in a smaller FB particle content compared with that in the preparation with a standard W/Bi ratio (0.55). It is probable that the solubility of Bi(OH)$_3$ under HT conditions is increased with higher pH to enhance particle growth by the Ostwald ripening mechanism. On the other hand, the percentage of non-FB particles (58%) obtained under condition (c) is slightly lower than the percentage of particles prepared under conditions (a) and (b) (though still higher than that of the standard sample (W/Bi ratio = 0.55), supporting the above-described hypothesis). The smaller size of particles under condition (c) than that under the standard conditions is attributable to the smaller molar amount of the tungsten source used for BTO flake growth.

The thus-created FB structure must have an influence on its photocatalytic activities. One of the merits of the FB structure is, as mentioned in the introductory part, a probable high crystallinity, i.e., low crystal-defect density, thus reducing the photoexcited electron–hole recombination. Another possible influence is photosorption properties depending on the FB structure, as was reported previously; the absorption edge (ca. 450 nm) of FB-BTO was ca. 30 nm red shifted compared with that of non-FB-BTO. This feature is now under investigation and will be reported elsewhere.

In conclusion, although further evidence, e.g., the presence of core Bi(OH)$_3$ particles in the early stage of HT reaction (see SI) is needed, the only possible reasonable mechanism, as far as the authors think, of the formation of characteristic hollow FB-structured BTO particles is the growth of BTO crystal plates on the surface of core particles by the supply of tungsten and bismuth from the outside and inside of the core particles, respectively. The elucidated mechanism of FB-particle formation, i.e., growth of plate-form crystallites from the spherical core particle surface, can be applied to the preparation of FB-like particles of highly crystallized plate assembly with a relatively high specific surface area, i.e., photocatalyst particles with a possible high level of photocatalytic activity.

Supporting Information is available electronically on J-STAGE.

References
Chemistry Letters – Supporting Information

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Composition analysis
Composition of samples was analyzed by X-ray diffractometry (XRD) and thermogravimetry. For XRD measurement, 0.300 g of sample and 0.075 g nickel oxide (NiO; Wako Pure Chemical) as an internal standard for crystalline composition analysis were mixed thoroughly in an agate mortar, set in a sample holder and measured using a Rigaku SmartLab diffractometer with an X-ray tube (copper K$_\alpha$) operated at 40 kV and 30 mA with scanning rate of 1.0 ° min$^{-1}$ and step of 0.02 ° in the 2θ range of 3–80°. Diffractograms were analyzed by PDNL including a RIETAN-FP Rietveld analysis package installed in the controlling personal computer. Assuming that NiO is 100% crystalline, i.e., without non-crystalline part, crystalline content of crystalline BTO was evaluated from the results of Rietveld analysis (F. Izumi and K. Momma, Solid State Phenom., 130, 15-20 (2007)). Content of water was analyzed by an ULVAC-Riko TGD-9700 thermogravimetry/differential thermal analysis instrument with an alumina sample holder under constant dry-air flow in the temperature range of 293–793 K. The content of water in samples was estimated by assuming that the weight loss by heating is only due to release of water.

Scanning electron microscopy
Morphology of products was observed by scanning electron microscopy (SEM) using a JEOL JSM-7400F field-emission SEM with acceleration voltage of 2.0–5.0 kV, 10.0 µA current and working distance of 6 mm in LEI detection mode. Sample powder was poured on a brass sample stage with conducting carbon tape and evacuated at 0.096 MPa overnight.
**Sonication**

Sonication post treatment was performed for a suspension of product underwent above-mentioned hydrothermal reaction with ca. 50-mL of an original acidic supernatant, Milli-Q water or aqueous sodium hydroxide (1 mol L$^{-1}$) in a 50-mL sample tube. In the latter two cases, 3-times washing with Milli-Q water was made before addition of water or aqueous sodium hydroxide. The suspension in a 50-mL glass tube was sonicated using a YAMATO–Branson 5510 ultrasonic cleaner (42 kHz; 180 W). Figure 2 (d)–(f) shows SEM images of samples sonicated in water for 30, 60 and 90 min. Sonication for 30 min did not give any appreciable change in the size of particles, while the thickness of flakes seemed to become slightly thinner. After 60-min sonication, some FB particles with a hole were observed and the 90-min sonicated sample contained broken FB particles with a void space inside.

BET specific surface area and pore structure of samples before and after sonication were evaluated based on the nitrogen adsorption at 77 K using a Quantachrome Autosorb-6B surface area and pore size analyzer. Specific surface area of an original FB sample was ca. 18–19 m$^{2}$ g$^{-1}$ and was negligibly changed by sonication, even though higher content of FB particles were decomposed to expose the inner vacant spaces, suggesting that the specific surface area of the original FB contained also the inner surface. For the pore volume measured simultaneously, slight increase from 0.13 to 0.16–0.18 cm$^{3}$ g$^{-1}$ was observed. It is presumed that the inner void spaces in the original FB particles were not counted as pores due to their micrometer size and the observed by sonication-induced increase in pore volume is attributable to spaces between degraded particles produced by sonication.

**Wet milling**

To a powder sample (1.8 g) and zirconia beads (0.3 mm; 14.4 g) in a 45-mL zirconia bottle (internal volume: 46.6 mL) was added 8.0-mL Milli-Q water, and the bottle was

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**Fig. S1** FE-SEM images of (a, b) lighter part (L) and (c, d) heavier part (H) of wet-milled FB-BTO particles.
set in a Fritsch Pulverisette 7 planetary ball mill to operate at 500 rpm for 6 h. The beads were separated with a sieve and washed with Milli-Q water, and suspension with the washing (ca. 200 mL in total) in two 110-mL glass tubes were sonicated using a YAMATO–Branson 5510 ultrasonic cleaner (42 kHz; 180 W) for 2 min. After standing for 25 min, upper parts (50 mL; containing relatively light particles "L") of the suspensions were separated from the lower part of suspensions (containing relatively heavy particles "H"), and particles L and H were collected by centrifugation at 3000 rpm for 30 min and drying in air at 393 K overnight.

**Comparison with BTO prepared by solid-state reaction**

Non-FB BTO particles were prepared by a solid-state reaction (SSR) of bismuth oxide and tungsten oxide in stoichiometric molar ratio at 1173 K. The non-FB structure of the thus-prepared sample was confirmed by SEM measurement (Fig. S2 (Right)). As shown in Fig. S2 (Left), bulk specific volume of FB-BTO (center) was ca. 4 times higher than that of SSR-BTO (left) and ca. 1.6 times higher than an ordinary micrometer-sized WO$_3$ powder (right).

![Fig. S2](Fig.S2.jpg)

**Fig. S2** Comparison of FB-BTO with BTO prepared by solid-state reaction (see text).

**Attempts for proof of the presence of core Bi(OH)$_3$ particles**

According to the proposed mechanism (Fig. 3), void space must be produced with the BTO-flake growth, and actually there have been obtained a few experimental results indicating the presence of a spherical void space in an FB-BTO particle. Since it is unlikely to that the FB particle-formation process is initiated by assembly of BTO plates/flakes leaving spherical void space inside, it seems reasonable to assume BTO plates/flakes grow from the surface of spherical precursor particles which provide a source of BTO and are consumed during the HT reaction. The most probable candidate of core particles is Bi(OH)$_3$ as suggested in the text. Several attempts were made to prove the presence of core Bi(OH)$_3$ particles.

One is an HT reaction without tungsten source; a suspension of Bi(OH)$_3$ (5.0 mmol) and sodium hydroxide (5.5 mmol), to adjust pH to be same as that in the standard procedure with sodium tungstate, in water (70 mL) was underwent HT treatment at 433 K for 20 h. SEM images of the product are shown in Fig. S3.
indicating the growth of non-spherical Bi(OH)$_3$ particles and their aggregation in the size of several tens micrometers. Although the size of those particles were larger than that expected from the FB-BTO particles according to the proposed mechanism, it is reasonable assuming that a tungsten component, H$_2$WO$_4$, may prohibit excess growth of Bi(OH)$_3$ under HT conditions by being deposited on the Bi(OH)$_3$ surface as BTO or WO$_3$.

Another attempt is cross-sectional SEM/TEM observation of particles at the early stage of HT reaction. At present, however, no reliable results have not been obtained, mainly due to the severe damage in the focused ion-beam (FIB) process for cross-sectional sample preparation.
Supporting Information

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![Fig. S2 Comparison of FB-BTO with BTO prepared by solid-state reaction (see text).](image)

**Attempts for proof of the presence of core Bi(OH)\(_3\) particles**

According to the proposed mechanism (Fig. 3), void space must be produced with the BTO-flake growth, and actually there have been obtained a few experimental results indicating the presence of a spherical void space in an FB-BTO particle. Since it is unlikely to that the FB particle-formation process is initiated by assembly of BTO plates/flakes leaving spherical void space inside, it seems reasonable to assume BTO plates/flakes grow from the surface of spherical precursor particles which provide a source of BTO and are consumed during the HT reaction. The most probable candidate of core particles is Bi(OH)\(_3\) as suggested in the text. Several attempts were made to prove the presence of core Bi(OH)\(_3\) particles.

One is an HT reaction without tungsten source; a suspension of Bi(OH)\(_3\) (5.0 mmol) and sodium hydroxide (5.5 mmol), to adjust pH to be same as that in the standard procedure with sodium tungstate, in water (70 mL) was underwent HT treatment at 433 K for 20 h. SEM images of the product are shown in Fig. S3.
indicating the growth of non-spherical Bi(OH)$_3$ particles and their aggregation in the size of several tens micrometers. Although the size of those particles were larger than that expected from the FB-BTO particles according to the proposed mechanism, it is reasonable assuming that a tungsten component, H$_2$WO$_4$, may prohibit excess growth of Bi(OH)$_3$ under HT conditions by being deposited on the Bi(OH)$_3$ surface as BTO or WO$_3$.

Another attempt is cross-sectional SEM/TEM observation of particles at the early stage of HT reaction. At present, however, no reliable results have not been obtained, mainly due to the severe damage in the focused ion-beam (FIB) process for cross-sectional sample preparation.