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Decahedral Single-Crystalline Particles of Anatase Titanium(IV) Oxide with High Photocatalytic Activity

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Enhancement of the photocatalytic efficiency of anatase titanium(IV) oxide (TiO_2) for decomposition of water and organic compounds has been a challenging subject. Electron−hole pairs, which are generated by band gap excitation of TiO_2, are transferred to surface-adsorbed reactants with competition of mutual recombination. Because recombination is expected to occur on grain boundaries and crystalline defects, use of single-crystalline particles with a low density of defects is one of the possible strategies. Indeed, single-crystalline anatase particles exhibited a high level of photocatalytic activity when they had a large specific surface area.[1] Miyauchi found that photoinduced hydrophilicity of a film composed of single-crystalline particles with predominantly exposed {101} facets was higher than that of a film composed of polycrystalline particles.[2] In general, well-developed anatase single crystals exhibited a (truncated) octahedral shape, i.e., tetragonal bipyramids, dominated by {101} facets, which are the most thermodynamically stable surface.[3−5] Interest has recently been shown in octahedral anatase particles with {101} facets.[2,6−8] On the other hand, preparation of single-crystalline anatase particles with a largely truncated octahedral shape with two square {001} facets, e.g., a decahedral shape, has been reported.[9,10] Because the {001} surface is more reactive for dissociative adsorption of reactant molecules compared with {101} facets,[11−15] high photocatalytic efficiency is expected for the particles with {001} facets,[16] though their photocatalytic activity has not been reported.

In the present study, we prepared single-crystalline anatase particles through a gas-phase reaction with relatively high yield of decahedral particles, the shape of which resembled those of particles prepared by hydrothermal reaction of titanium tetrafluoride (TiF_4) in acidic conditions in a study by Lu and co-workers.[9] It has been recognized that photocatalytic efficiency depends on surface area, if the reaction rate is expressed by first-order kinetics with respect to the amount of surface-adsorbed reactants and the amount increases with an increase in surface area. Therefore, the smaller size of the present particles is preferable for photocatalytic reactions. Herein, we report the photocatalytic activity of single-crystalline anatase TiO_2 particles with reactive {001} facets, the size of which was much smaller than that of particles prepared by hydrothermal reaction of TiF_4 (>1 μm).[9]

TiO_2 crystallites were fabricated from titanium(IV) chloride ($TiCl_4$) by a gas-phase reaction process with rapid heating and quenching.[17] The vapor of $TiCl_4$ was liberated by bubbling argon (200 mL min^{-1}) into a $TiCl_4$ solution at 358 K, mixing it with an oxygen stream (1200 mL min^{-1}), and feeding into a quartz glass tube heated from the outside by an oxyhydrogen flame burner. The tube was rotated around the cylindrical axis at a speed of 55 rpm for homogeneous heating. The heating temperature was adjusted to 1573 K. The TiO_2 particles generated by thermal oxidation of $TiCl_4$ were collected at the down stream by a filter cup made of glass fibers. Uniform and rapid heating at a high temperature would enable homogeneous nucleation and subsequent growth to well faceted crystals with few defects. The low concentration of $TiCl_4$ and the narrow heating zone would prevent formation of large particles and polycrystalline aggregates with grain boundaries.

Figure 1 shows a scanning electron microscopic (SEM) image of the prepared TiO_2 particles consisting of mainly decahedral particles, i.e., truncated bipyramids. The averaged aspect ratio (B/A),[18] which is defined by the ratio of

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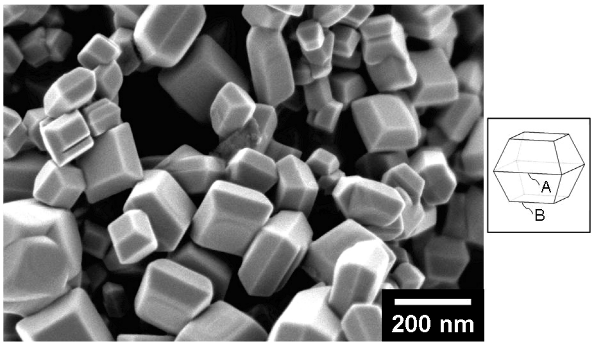

Figure 1. SEM image of TiO_2 particles prepared by gas-phase reaction of $TiCl_4$ with oxygen.

short (*B*) and long (*A*) sides, was ca. 0.65−0.75. This value is smaller than that of the decahedral particles prepared by Lu and co-workers, ca. 0.8 corresponding to nearly 40% exposure of {001} facets to the total exposed facets.[9] Although the particle size was not regular, the size of 50−250 nm was much smaller than that of the decahedral particles prepared previously.[9] The BET specific surface area was found to be 9.4 $m^2\ g^{-1}$ by nitrogen adsorption measurement. The powder X-ray diffraction pattern indicated that there are anatase crystallites and a small amount of contamination of rutile crystallites (see Figure S1 in the Supporting Information). Kauppinen and co-workers also reported that gas-phase crystallization of titanium(IV) tetra-2-propoxide at 1473 K involves formation of minor rutile crystallites in addition to single-crystalline anatase particles with {101} and {001} facets.[10]

Figure 2 shows transmission electron microscopic (TEM) images of the decahedral anatase particles. Because anatase crystal is of a tetragonal system (JCPDS card No. 21−1272), the square-shaped particle indicates that the {001} facet of the particle was mounted in parallel to a sample grid (Figure 2A). The electron diffraction pattern, indicating that the particle is a single crystal, was consistent with the expected direction. A high-resolution TEM image shows interplanar spacing of (200) and (020). The equal-thickness fringes observed at the edge of the square-shaped particle indicate the presence of slopes due to {101} facets. Figure 2B shows another particle of single-crystalline anatase recorded by incident beam direction perpendicular to {100}. An angle of ca. 68.3°, which is consistent with the interfacial angle between (001) and (101), was observed on the hexagonal-shaped particle, suggesting that the particle exhibits flat surfaces of {001} and {101}.

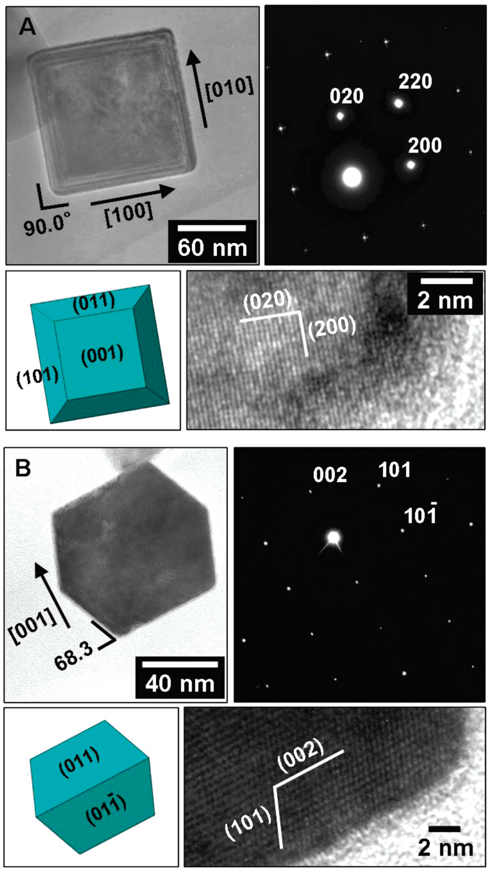

Figure 2. TEM images and electron diffractions of decahedral TiO_2 particles recorded along (A) the *c*-axis and (B) the *a*- or *b*- axis.

The photocatalytic activity of the decahedral single-crystalline (DSC) particles was evaluated by reaction of hydrogen (H_2) evolution from an aqueous solution of methanol. Commercial TiO_2 powder, P25 (Nippon Aerosil),[19] was used as a reference. A suspension containing photocatalysts powder (50 mg) and precursors for in situ photodeposition of platinum (Pt; 2 wt %) nanoparticles was irradiated by a 400 W high-pressure mercury lamp under deaerated conditions. In the absence of Pt, no appreciable H_2 evolution was detected for any of the tested samples. Figure 3 shows timecourses of the photocatalytic H_2 evolution. Using hydrogen hexachloroplatinate(IV) (H_2PtCl_6) as a Pt precursor, a linear increase in the amount of H_2 with irradiation time was observed. The rate of H_2 evolution by DSC particles was higher than that by P25. P25 is one of the best photocatalysts for this reaction among the commercial TiO_2 photocatalysts,[20] and only a small number of prepared TiO_2 samples show activity higher than that of P25.[21] When tetraammineplatinum(II) chloride ($[Pt(NH_3)_4]Cl_2$) was used as a Pt precursor instead of H_2PtCl_6, the rate of H_2 evolution was decreased and an induction period of ca. 30 min was observed for both types of TiO_2. This induction period might be due to the possible difficulty in reduction or less adsorption of $[Pt(NH_3)_4]Cl_2$ than that of H_2PtCl_6. The steady-state rate of H_2 evolution by DSC particles was much higher than that by P25. It has been reported that an anatase {001} surface is much more reactive for dissociation of water and methanol than is a {101} surface, on which molecules are adsorbed without dissociation.[11−15] The high level of photocatalytic activity of DSC particles might be related to the property of the exposed {001}

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(19) P25 contains anatase crystallites and small portion of rutile crystallites (see Figure S1 in the Supporting Information). The BET specific surface area was measured to be 48 $m^2\ g^{-1}$.

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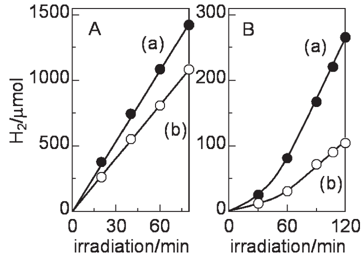

Figure 3. Photocatalytic H_2 evolution from an aqueous solution of 50 vol % methanol under an Ar atmosphere in the presence of (A) H_2PtCl_6 and (B) $[Pt(NH_3)_4]Cl_2$ containing (a) DSC particles and (b) P25.

surface, which is not selectively exposed in the case of usual anatase crystallites, in addition to the high crystallinity with a low density of defects in DSC.

Ohno et al. reported that Pt particles were preferably deposited on micrometer-sized decahedral anatase particles in the order of {101} > {001}≫{112} in photocatalytic reduction of H_2PtCl_6 using 2-propanol as an electron donor.[22,23] In the present study, it was also observed that Pt particles were deposited both on {101} and {001} facets, as seen in secondary electronic images of DSC particles after photocatalytic H_2 evolution (see Figure S2 in the Supporting Information).

Figure 4 shows time courses of the photocatalytic oxidative decomposition of organic compounds (acetic acid and methanol) in an aerated aqueous suspension (see the Supporting Information). The amount of CO_2 linearly increased with irradiation time for acetic acid decomposition. The DSC particles exhibited a rate of CO_2 liberation as high as that of P25, which is the one of the best photocatalysts for this reaction.[20] In the case of decomposition of methanol, the amount of CO_2 liberation over DSC particles was much larger than that of P25. The difference between the photocatalytic activity of DSC particles and that of P25 seems significant for methanol decomposition rather than acetic acid decomposition. It should be noted that white P25 particles turned blue immediately after commencement of photoirradiation during photocatalytic methanol oxidation, which was not the case for DSC particles. The blue color is attributable to the formation of reduced species of Ti^{4+} (Ti^{3+}).[24] This indicates that electrons are accumulated in P25 particles even in the presence of molecular oxygen as an electron acceptor. Efficient electron transfer to oxygen at the surface of DSC particles may account for their better or comparable photocatalytic activity.

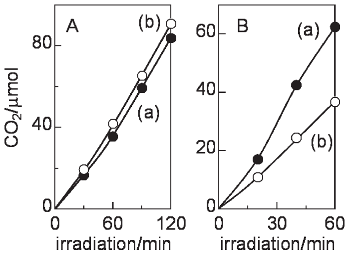

Figure 4. Photocatalytic CO_2 liberation from an aqueous solution of (A) 5 vol% acetic acid and (B) 50 vol% methanol under air containing (a) DSC particles and (b) P25.

In conclusion, faceted decahedral single-crystalline anatase particles (DSC) with sizes of 50−250 nm have been fabricated for the first time by a newly developed gas-phase process using $TiCl_4$ as a titanium source. Although DSC has a relatively small specific surface area (9.4 $m^2 g^{-1}$) compared with that of P25 (48 $m^2 g^{-1}$) as a de facto standard, the photocatalytic activity was higher than or at least comparable to that of P25 for reactions operated under various conditions.[25] Low density of crystalline defects might be the reason for the extremely high photocatalytic activity for H_2 evolution from an aqueous methanol solution and oxidative decomposition of organic compounds in an aqueous solution. Further systematic comparison of the photocatalytic activities of decahedral particles with different aspect ratios and different specific surface areas will provide detailed information on factors affecting photocatalytic activities. Study along this line is now in progress.

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Supporting Information Available: Experimental details of photocatalytic reactions, apparent quantum efficiencies, X-ray diffraction patterns, and secondary electron images of Pt-loaded decahedral TiO_2 particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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