Photocatalytic activity of octahedral single-crystalline mesoparticles of anatase titanium(IV) oxide†

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Octahedral titanium(IV) oxide (TiO₂) crystallites with exposed anatase {101} facets exhibited relatively high photocatalytic activity for oxidative decomposition of organic compounds and low activity for hydrogen evolution in the absence of molecular oxygen, probably due to the characteristics of the anatase {101} surface.

Anatase has been the most extensively studied polymorph of TiO_2 owing to its high photocatalytic activity for oxidative decomposition of organic compounds in the presence of molecular oxygen,[1,2] and hydrogen (H_2) evolution. Surface free energy of the anatase {101} lattice plane has been reported to be the smallest among the planes of anatase.[3] In agreement with natural minerals, a truncated octahedral bipyramid, exposing eight {101} facets as well as two {001} facets, has been shown to be the most thermodynamically stable shape of anatase crystallites based on Wulff construction.[3] In spite of the important applications of anatase TiO_2, experimental studies on the photoactive property of a single-crystalline surface have been limited due to the difficulty in obtaining high-quality anatase samples.[4] A few studies have suggested a significant role of facets of TiO_2 polyhedral particles for photocatalytic reactions.[5] Recent developments of hydrothermal reaction methods have enabled the preparation of anatase crystalline particles with well-developed facets in a relatively high yield.[6]

In the present study, we investigated the roles of {101} facets, which are most likely to be observed on anatase mesoparticles,[7] for practical photocatalytic reaction systems such as powder suspensions. In order to compare the photocatalytic activity of well-defined anatase single-crystal particles with that of commercial TiO_2 photocatalyst powders, the crystalline size should be on the submicrometre scale, mesoparticles, in order to have a surface area comparable to that of commercial powders. We have found that

hydrothermal reaction of titanate nanowires yielded mesoparticles of anatase octahedral bipyramids. Their photocatalytic activity for oxidative decomposition of organic compounds and H_2 evolution from an aqueous methanol (MeOH) solution was investigated to clarify the photocatalytic property of anatase {101} surfaces.

Titanate nanowires were prepared by hydrothermal reaction of TiO_2 particles, P25 (Nippon Aerosil), in a 17 mol L^{-1} potassium hydroxide solution at 383 K for 20 h.[8] The nanowires (100 mg) were stirred in MilliQ-water (30 mL) and heated in a Teflon-lined autoclave (100 mL) at 443 K for 24 h. The white precipitates were centrifuged and dried at 393 K. Fig. 1a–c show scanning electron microscopy (SEM) images of titanate nanowires before and after hydrothermal reaction at 443 K. The typical diameters and lengths of titanate nanowires were 5–15 nm and several hundreds of nanometres, respectively.[8] Analysis using energy dispersive X-ray spectroscopy revealed the presence of potassium ion in titanate nanowires (atomic ratio of potassium to titanium of *ca.* 12%). Specific surface area (SSA) of titanate nanowires was *ca.* 400 m² g⁻¹. Hydrothermal reaction of titanate nanowires resulted in production of mesoparticles of an octahedral morphology, *i.e.*, bipyramidal shape, and the sizes of the long axis were <100 nm. The proportion of regular octahedral bipyramids in the particles was *ca.* 70%. The remaining particles were also similar to octahedral bipyramids while the shape was rounded or irregular, suggesting the presence of high-index lattice planes. The particles were revealed by
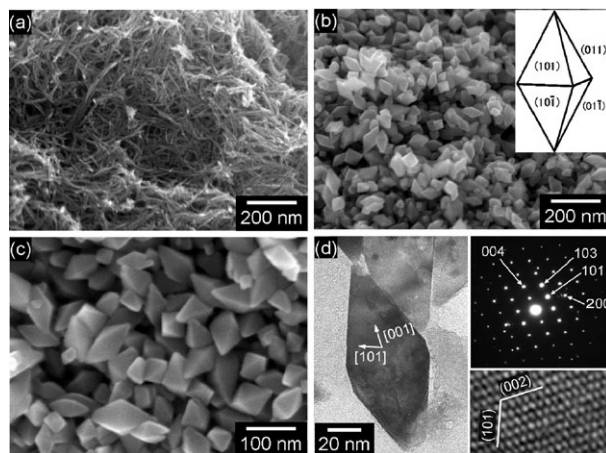
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Fig. 1 SEM image of (a) titanate nanowires and (b, c) particles after hydrothermal reaction of titanate nanowires. (d) TEM image and electron diffraction pattern of an octahedral bipyramid.

high-resolution transmission electron microscopy (TEM) and selected area electron diffractometry to be single crystals of anatase TiO_2 (Fig. 1d and Fig. S1 in ESI†). The orientation of fringes, *i.e.*, crystal direction, was consistent to that of the equilibrium shape of anatase crystallites. The octahedral bipyramids exhibited predominantly anatase {101} facets, while the edges of crystallites became rounded to some extent and other facets such as {100} were also exposed. Fig. 2 shows X-ray diffraction patterns of titanate nanowires before and after hydrothermal reaction. The titanate phase was completely converted to anatase TiO_2 crystallites by the hydrothermal reaction. There seemed to be no other TiO_2 polymorphs such as rutile. SSA of the anatase particles containing octahedral crystallites was 40 m^2 g^{-1}.

When another source, tightly bound titanate nanowires, was employed as a precursor, larger octahedral particles (SSA of 25 m^2 g^{-1}) were obtained, and the sizes of the particles were not uniform. The proportion of octahedral bipyramids was *ca.* 60%, less than that of particles prepared from less-bundled titanate nanowires. This indicates that the nanowire structure influences the process of octahedral crystallite production.

Photocatalytic activity for oxidative decomposition of organic compounds was evaluated by carbon dioxide liberation rate ($r(CO_2)$) from an aerated aqueous suspension (5.0 mL) containing a photocatalyst (50 mg) under irradiation by a 400 W high-pressure mercury lamp (>290 nm) at 298 K. Fig. 3 shows the relationship between photocatalytic activities in decomposition of acetic acid (AcOH, 5 vol%) and MeOH (50 vol%) containing hydrothermally-prepared mesoparticles, P25 (composite of anatase (main) and rutile), and 19 types of commercial anatase TiO_2 particles, JRC-TIO-1, 2, 7, 8, 9, 10, 12 and 13 (Catalysis Society of Japan), ST-01, 21 and 41 (Ishihara Sangyo), PC-101 and 102 (Titan Kogyo), TKP-101 and 102 (Tayca), and Hombikat UV100 (Sachtleben Chemie). The $r(CO_2)$ in MeOH decomposition was lower than $r(CO_2)$ for AcOH decomposition over all TiO_2 photocatalysts. P25 and mesoparticles containing octahedral crystallites exhibited higher photocatalytic activity than those of commercial anatase TiO_2 particles for both reactions. The $r(CO_2)$ in MeOH decomposition was increased with an increase of $r(CO_2)$ in AcOH decomposition. We could not find any relationship between SSA and photocatalytic activity for oxidative decomposition of organic compounds among the series of anatase TiO_2 samples. This may be because the

Fig. 3 Relationship between photocatalytic activities for oxidative decomposition of AcOH and MeOH: (a, b) mesoparticles containing octahedral crystallites prepared from (a) titanate nanowires and (b) bundled titanate nanowires, (c) P25, and (open circles) commercial anatase TiO_2 particles.

activity depends on both SSA and density of lattice defects,[9] and, in general, particles with large SSA exhibits high density of surface lattice defects, which enhance recombination of photogenerated carriers. It has been reported that P25 contains mainly faceted anatase crystallites exposing {010}, {101} and {001} facets, the former one probably being more abundant than the other two.[10] The higher $r(CO_2)$ of octahedral mesoparticles and P25 indicates the importance of a well-crystallized surface for high level of photocatalytic activity for decomposition of organic compounds.

Fig. 4 shows the relationship between photocatalytic activities for oxidative decomposition of MeOH and for dehydrogenation of MeOH. Photocatalytic dehydrogenation activity was evaluated by H_2 evolution rate ($r(H_2)$) from a deaerated aqueous 50 vol% MeOH solution containing hexachloroplatinic acid as a precursor of photodeposition of 2.0 wt% platinum (Pt). The $r(H_2)$ of commercial anatase TiO_2 particles seemed to increase with an increase in $r(CO_2)$ from a MeOH solution. For both reactions, P25 exhibited the highest photocatalytic activities. Although $r(CO_2)$ of the mesoparticles containing octahedral crystallites was relatively high, $r(H_2)$ from a MeOH solution was much lower than those of P25 and most of the commercial anatase TiO_2 particles. For commercial anatase particles, since there was a tendency for
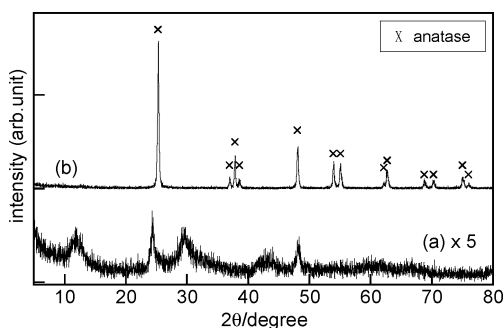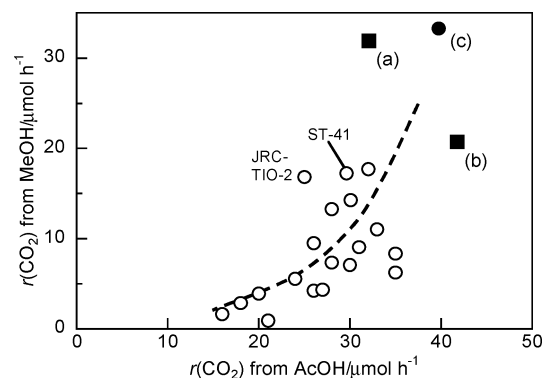

Fig. 2 XRD patterns of (a) titanate nanowires and (b) particles after hydrothermal reaction of titanate nanowires. Pattern (b) was translated along the Y-axis for clarity.
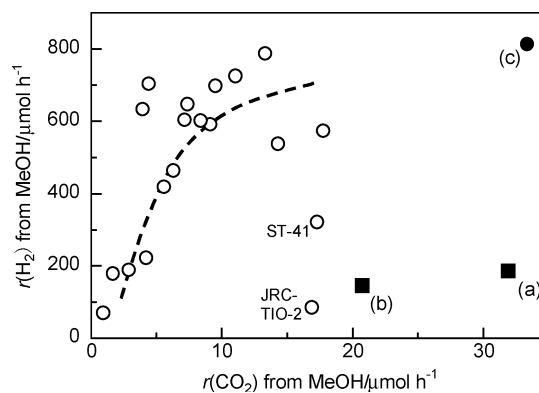

Fig. 4 Relationship between photocatalytic activities for oxidative decomposition and dehydrogenation of MeOH. Symbols are the same as those in Fig. 3.

samples of high $r(CO_2)$ from a MeOH solution to show high $r(H_2)$ from a MeOH solution, the relatively low $r(H_2)$ of octahedral mesoparticles seems strange. In contrast to photocatalytic dehydrogenation, photocatalytic oxidative decomposition was performed under aerated conditions, suggesting that photocatalytic activities were different in the reactions with and without molecular oxygen for octahedral crystallites. Considering the predominant exposure of {101} facets on octahedral crystallites, it has been proposed that reduction of molecular oxygen by photoexcited electrons and oxidation of organic compounds by positive holes are easily promoted on {101} surface. However, we could not completely exclude the possibility that less abundant facets and lattice planes exhibited much higher activity than that of {101} facets.

In the case of photocatalytic dehydrogenation of MeOH, $r(H_2)$ over anatase particles with small SSA was lower than that over nanoparticles with large SSA (Fig. S2, ESI†). The SSA of the mesoparticles containing octahedral crystallites (25–40 m^2 g^{-1}) was smaller than those of commercial anatase particles. Therefore, one of the reasons for the low $r(H_2)$ over mesoparticles containing octahedral crystallites is their relatively small SSA. In general, crystals are grown in the direction that minimizes overall surface free energy, and higher energy facets disappear with an increase in crystalline size,[11] so that, anatase particles with small SSA would predominantly expose low index facets with small energy. However, it is difficult to conclude the reason for the relatively low $r(H_2)$ over anatase particles with small SSA, because P25 exhibited high $r(H_2)$ despite the relatively small SSA. Another important point is that photocatalytic dehydrogenation of MeOH was performed in the presence of hexachloroplatinic acid, which is reduced by photoexcited electrons to give Pt nanoparticles on TiO$_2$. In the absence of Pt, H$_2$ evolution over anatase particles was negligible. Therefore, $r(H_2)$ would be influenced by not only the property of anatase crystallites but also the property of deposited Pt nanoparticles. Particularly in a low loading region, the photocatalytic activity for H$_2$ evolution may strongly depend on the state of deposited Pt particles. However, the dosage amount of Pt (2.0 wt%) seemed sufficient in the present study. We confirmed the deposition of Pt nanoparticles on octahedral bypyramids after photocatalytic dehydrogenation (Fig. S6, ESI†). Furthermore, it was also confirmed that the Pt-loaded samples exhibited photocatalytic activity 3.4-times higher than that of the bare octahedral crystallites for oxidative decomposition of AcOH (Fig. S7, ESI†). Thus, the low $r(H_2)$ over mesoparticles containing octahedral crystallites is not attributable to the difference in the state of Pt nanoparticles but to the difference between properties of anatase {101} facets and those of others. Actually, theoretical and experimental studies have revealed that the anatase {101} surface is less favorable for dissociative adsorption of water and MeOH to result in molecular non-dissociative adsorption.[12] The flatband potential of the {101} surface has been reported to be located positively by ca. 0.06 eV than that of the {001} surface, on which water molecules are dissociatively chemisorbed.[13] Although the energy level of the conduction band bottom is one of the decisive factors for H$_2$ evolution, the difference in flatband potentials seems small among anatase lattice planes. Therefore, the low $r(H_2)$ of octahedral crystallites might be due to the surface structure of anatase {101}, which would affect the reaction mechanism at the molecular level, rather than the conduction band level.

In conclusion, both the preparation of anatase crystallites having a particular facet and the evaluation of their photocatalytic activity in a practical powder-suspension system provided a new insight into the photocatalytic property of anatase single-crystalline facets. It was shown that the anatase crystallites with abundant {101} facets are effective for photocatalytic oxidative decomposition of organic compounds in the presence of molecular oxygen. On the other hand, it was suggested that the anatase {101} surface is not as effective as other surfaces exposed on ordinary anatase particles for H$_2$ evolution in the absence of molecular oxygen. Preparation of perfect octahedral crystallites without any other lattice planes and comparison of the photocatalytic activity with that of crystallites exposing {101} and another facets will provide further information and obvious evidence on the roles of specific lattice planes of anatase TiO$_2$ for photocatalytic reactions.

Notes and references

1 T. Ohno, K. Sarukawa and M. Matsumura, *J. Phys. Chem. B*, 2001, **105**, 2417.

2 T. Torimoto, N. Nakamura, S. Ikeda and B. Ohtani, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5910.

3 (a) M. Lazzeri, A. Vittadini and A. Selloni, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 155409; (b) U. Diebold, N. Ruzycki, G. S. Herman and A. Selloni, *Catal. Today*, 2003, **85**, 93.

4 L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz and H. J. Scheel, *J. Am. Chem. Soc.*, 1996, **118**, 6716.

5 (a) T. Ohno, K. Sarukawa and M. Matsumura, *New J. Chem.*, 2002, **26**, 1167; (b) T. Taguchi, Y. Saito, K. Sarukawa, T. Ohno and M. Matsumura, *New J. Chem.*, 2003, **27**, 1304.

6 (a) H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng and G. Q. Lu, *Nature*, 2008, **453**, 638; (b) D. H. Wang, J. Liu, Q. S. Huo, Z. M. Nie, W. G. Lu, R. E. Williford and Y. B. Jiang, *J. Am. Chem. Soc.*, 2006, **128**, 13670; (c) E. Hosono, S. Fujihara, H. Imai, I. Honma, I. Masaki and H. S. Zhou, *ACS Nano*, 2007, **1**, 273.

7 V. Shklover, M. K. Nazeeruddin, S. M. Zakeeruddin, C. Barbe, A. Kay, T. Haibach, W. Steurer, R. Hermann, H. U. Nissen and M. Grätzel, *Chem. Mater.*, 1997, **9**, 430.

8 (a) S. Uchida and Y. Sanehira, *Jpn. Pat.*, P2005-162584A, 2005; (b) F. Amano, T. Yasumoto, T. Shibayama, S. Uchida and B. Ohtani, *Appl. Catal., B*, 2009, DOI: 10.1016/j.apcatb.2009.01.013.

9 F. Amano, K. Nogami and B. Ohtani, *J. Phys. Chem. C*, 2009, **113**, 1536.

10 G. Spoto, C. Morterra, L. Marchese, L. Orio and A. Zecchina, *Vacuum*, 1990, **41**, 37.

11 (a) R. L. Penn and J. F. Banfield, *Geochim. Cosmochim. Acta*, 1999, **63**, 1549; (b) Y. W. Jun, M. F. Casula, J. H. Sim, S. Y. Kim, J. Cheon and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2003, **125**, 15981.

12 (a) G. S. Herman, Z. Dohnalek, N. Ruzycki and U. Diebold, *J. Phys. Chem. B*, 2003, **107**, 2788; (b) Tilocca and A. Selloni, *J. Phys. Chem. B*, 2004, **108**, 19314; (c) X. Q. Gong and A. Selloni, *J. Phys. Chem. B*, 2005, **109**, 19560.

13 R. Hengerer, L. Kavan, P. Krtil and M. Grätzel, *J. Electrochem. Soc.*, 2000, **147**, 1467.