Crystal faces of rutile and anatase TiO_2 particles and their roles in photocatalytic reactions

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A titanium dioxide powder consisting of 1 μm size rutile and anatase particles was obtained, on which developed crystal faces were observed by a scanning electron microscope. From electron diffraction analyses, it was found that the rutile particles exposed {011} and {110} crystal faces, and the anatase particles exposed {001} and {011} faces. This powder showed high activity for some photocatalytic reactions, including oxidation of water. After photocatalytic oxidation of water on the powder using hexachloroplatinate(IV) ions as the electron acceptors, Pt deposits were observed mostly on the rutile particles, especially on the {110} face. When 2-propanol was added to the solution, Pt was deposited on both the anatase and rutile particles. Using the thus prepared Pt-deposited TiO_2 powder, Pb^{2+} ions were photocatalytically oxidized into PbO_2. After this reaction, PbO_2 deposits were seen on the {011} face of the rutile particles. On the anatase particles, PbO_2 deposits were observed in a larger amount on the {001} face than on the {011} face. These results indicate that the crystal faces help in the separation of electrons and holes, and that this effect is stronger for the rutile particles than for the anatase particles.

Photocatalytic reactions on TiO_2 powders have attracted much attention because of their applicability to the treatment of a variety of pollutants[1–6] and to the chemical conversion of solar energy.[7–11] In these reactions, electrons and holes photogenerated in TiO_2 particles migrate to the surface, to reduce and oxidize compounds included in water and air. In order to deepen the understanding of the mechanisms of photocatalytic reactions, it is very important to identify the actual reactive sites of TiO_2 particles. Photoelectrochemical properties of different crystal faces on rutile TiO_2 single crystal electrodes have been reported.[12,13] Photocatalytic activities of the crystal faces of single crystalline rutile films[14] and crystallites on polycrystalline rutile ceramics[15] were also reported. However, in the case of anatase TiO_2, only limited information is available[16] because it is difficult to synthesize anatase single crystals and cereamics. It is also difficult to synthesize large TiO_2 particles with developed crystal faces. As a result, very limited information on the effect of crystal faces of particulate TiO_2 photocatalysts is available.[17] Here, we report the effect of crystal faces of rutile and anatase TiO_2 particles on the photocatalytic activity.

Experimental

We obtained various kinds of TiO_2 powders from Toho Titanium Co. The TiO_2 powders were synthesized by oxidation of titanium tetrachloride under different conditions. Among the powders, we found one lot which consisted of anatase and rutile particles with developed crystal faces. The amounts of the anatase and rutile phases of this powder were determined to be 85% and 15%, respectively, from the X-ray diffraction (XRD) patterns obtained by using an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target Kα-ray ($\lambda = 1.5405$ Å). The relative surface area was determined to be 1.1 $m^2 g^{-1}$ by the BET method using a surface area analyzer (Micromeritics, FlowSorb II 2300). The morphologies of the TiO_2 powders were examined by using a Hitachi H-800 transmission electron microscope (TEM) and a Hitachi S-5000 scanning electron microscope (SEM).

Photocatalytic reactions were carried out in Pyrex flasks (100 mL) containing reaction solutions (50 mL) and the TiO_2 powder. During the reactions, the TiO_2 powder was suspended in the solution by a magnetic stirrer. A 500 W super-pressure Hg lamp (Wacom, BMO-500DY) was used as the light source, and the irradiation intensity was controlled using fine stainless meshes as neutral density filters. Photocatalytic oxygen evolution and hydrogen evolution reactions were carried out in an argon atmosphere, and the amounts of the evolved gasses were quantitatively determined from the analyses of the components of the gas phase by gas chromatograpy.

Results and discussion

SEM and TEM observations of TiO_2 powders

Fig. 1 shows typical SEM and TEM images of rutile (a) and anatase (b) particles included in the TiO_2 powder. The average size of the rutile and anatase particles is about 1 μm. The rutile particle shows a tetragonal prism structure with four planes, which are assigned to the {110} faces. Each end of the prism is capped by four planes, which are assigned to the {011} faces. The anatase particle has a tetragonal bipyramid structure consisting of eight {011} faces. Both vertexes are removed and capped by the {001} faces. These {001} faces are usually convex, especially near the edges. All these crystal faces were assigned from the electron diffraction patterns as shown in Fig. 1, based on the reported lattice parameters.[18,19]

Photocatalytic activity of the TiO_2 powder

By measuring the photocatalytic activities of the TiO_2 powder and some other TiO_2 powders commonly used in the field of

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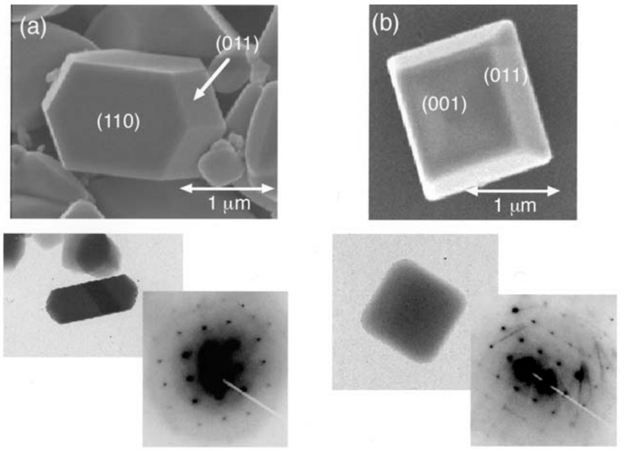

Fig. 1 SEM and TEM images, and electron diffraction patterns (from top to bottom) of a rutile particle (a) and an anatase particle (b) included in the TiO_2 powder.

photocatalysis, we found that the present TiO_2 powder is one of the most active photocatalysts for oxidation of 2-propanol in water, if the UV intensity is low (lower than 0.5 mW cm^{-2}) and the concentration of 2-propanol is high (higher than 0.1 M). Under such conditions, it is considered that the reaction rate is not determined by the surface area of the TiO_2 powder, but by more fundamental properties, such as the rate of electron-hole recombination, catalytic activity of the surface, *etc.*[20] This TiO_2 powder also shows fairly high photocatalytic activity for the oxidation of water when Fe^{3+} ions are used as the electron acceptors, although it is less active than large rutile particles.[21] For this reaction, large rutile particles show high activity, while commercial anatase particles, which are usually very small, show practically no activity.[21]

Photocatalytic oxidation of water and platinum deposition on the TiO_2 powder

We photocatalytically oxidized water on the TiO_2 powder using $PtCl_6{}^{2-}$ as an electron acceptor, and tried to observe Pt particles deposited on the TiO_2 by SEM. When the reaction was carried out under strong UV-irradiation, the reaction finished in a short time and Pt particles were deposited only on a small part of the particles, probably because the Pt deposition occurred on the strongly irradiated particles. We therefore carried out the reaction under weak UV-irradiation (about 0.2 mW cm^{-2}) for a long time period so that the particles were irradiated homogeneously. The irradiation was continued for 53 h in an evacuated 100 mL flask, which contained an aqueous solution of 1 mM H_2PtCl_6 (50 mL) and TiO_2 powder (1.0 g). After washing the UV-irradiated TiO_2 particles with water, we took SEM images of the TiO_2 particles. As shown in Fig. 2(a), many small Pt particles are deposited on the rutile particles, while few Pt deposits are seen on the anatase particles. Since Pt deposition is the counter reaction of water oxidation on the TiO_2 particles, we conclude that rutile particles are active for water oxidation, but anatase particles are not. It has been known that small anatase particles are inactive for oxidation of water.[21] The result shown in Fig. 2(a) strongly suggests that the anatase particles have poor activity for this reaction, even if their particle size is as large as 1 µm.

Fig. 2(b) is a view of one rutile particle, which shows that the Pt particles are deposited only on the {110} face. The same tendency is also observed on the rutile particles seen in Fig. 2(a). These results indicate that the reduction site of rutile TiO_2particles exists on the {110} face.

When 2-propanol (0.52 M) was added to the solution, Pt deposition was enhanced because 2-propanol is oxidized more easily than water. Fig. 3 depicts the SEM image of an anatase particle (center) and a rutile particle (right) after running the photocatalytic reaction for 24 h. In this case, Pt fine particles are seen not only on the rutile particle but also on the anatase particle. This means that the anatase particles can oxidize 2-propanol, although they can hardly oxidize water. Note that the Pt deposits on the anatase particle are seen in a larger amount on the {011} face than on the {001} face. This result suggests that the {011} face of anatase TiO_2 particles is more reductive than the {001} face, although the difference between these faces is smaller than the difference between the {110} and {011} faces of rutile particles.

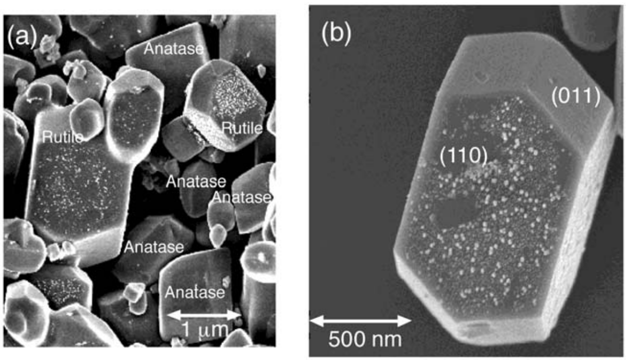

Fig. 2 SEM images of TiO_2 particles on which Pt fine particles were deposited by UV-irradiation in a solution of 1.0 mM H_2PtCl_6; (a) rutile and anatase particles, (b) a rutile particle. Note that Pt is deposited on the {110} face of rutile TiO_2 particles.

Photocatalytic deposition of PbO_2 on the TiO_2 powder

We used the TiO_2 powder, on which Pt was deposited by photoirradiation in the solution containing 2-propanol, as the photocatalyst. Using this platinized TiO_2 powder (1.0 g), we oxidized Pb^{2+} ions into PbO_2. This reaction was carried out in a 100 mL flask containing a 0.1 M $Pb(NO_3)_2$ solution (50 mL) under aerated conditions. The pH of the solution for this reaction was adjusted at 1.0 by the addition of nitric acid according to the literature.[22] After photoirradiation for 24 h, the color of the powder changed to brown, suggesting that PbO_2 was deposited on the surface. The deposition of PbO_2 was confirmed by the appearance of a new XRD peak ($2\theta = 32.0$ degrees), which is due to the diffraction by the (101) plane of crystalline PbO_2.[23]

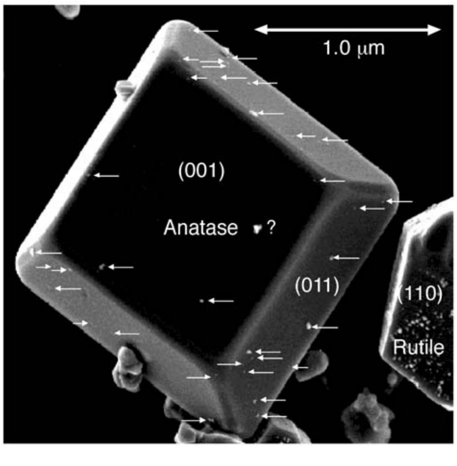

Fig. 3 SEM image showing an anatase particle (center) and a rutile particle (right). On these particles, Pt fine particles were deposited by UV-irradiation in an aqueous solution containing 1.0 mM H_2PtCl_6 and 0.52 M 2-propanol. Arrows on the anatase particle indicate the Pt deposits.

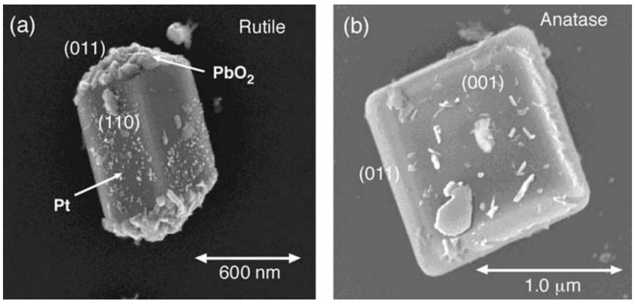

Fig. 4 SEM images of a rutile particle (a) and an anatase particle (b) showing PbO_2 deposits, which were loaded on the particles by UV-irradiation of the Pt-deposited TiO_2 powder in a solution of 0.1 M $Pb(NO_3)_2$. Prior to the deposition of PbO_2, Pt fine particles were deposited on the TiO_2 particles by a photocatalytic reaction in a solution containing 1.0 mM H_2PtCl_6 and 0.52 M 2-propanol.

The rate of PbO_2 deposition was slow when the reaction was carried out using TiO_2 powder without deposited Pt particles. The rate was also slow when oxygen was removed from the solution. In this case, hydrogen was observed in the gas phase of the flask after the reaction. Hence, it is considered that oxygen dissolved in the solution accepts electrons from TiO_2 *via* the Pt fine particles when Pb^{2+} ions are oxidized into PbO_2 on the TiO_2 particles.

SEM images depicted in Fig. 4 show that the PbO_2 particles are deposited on both rutile (a) and anatase (b) particles. On the rutile particles, they are seen mostly on the {011} faces. This means that the {011} face provides the oxidation site for rutile particles. On the anatase particles, the PbO_2 deposits are observed on both the {001} and {011} faces. The amount is larger on the former face than on the latter face, suggesting that the {001} face is more oxidative than the {011} face.

Oxidation and reduction sites on TiO_2 particles

The results shown in Figs. 2–4 indicate that the oxidation site and the reduction site on the rutile particles are on the {011} face and on the {110} face, respectively. For anatase particles, it is suggested that the oxidation site is mainly on the {001} face and the reduction site is mainly on the {011} face.

Farneth *et al.*[17] observed fine Ag particles photocatalytically deposited on about 300 nm size rutile particles by atomic force microscopy. Although the crystal faces on the TiO_2 particles are not clear, they concluded that the fine Ag particles are mostly deposited on the {110} face. This conclusion agrees with ours obtained for the deposition Pt particles. In contrast, the study done by Hotsenpiller *et al.*[14,15] led to completely different conclusions. They reported that Ag particles are photocatalytically deposited at higher velocities on the {001} and {011} faces than on the {110} and {010} faces. In their study, they used single crystalline rutile films[14] and crystallites of polycrystalline rutile ceratimcs.[15] In the case of the single crystalline films, both oxidation and reduction reactions have to occur on the same crystal face because only one crystal face is exposed. The situation of the polycrystalline ceramics is similar to that of the single crystalline films because the size of the crystallites was very large (about 55 μm). In these cases, the evaluated photocatalytic activity is for the isolated crystal faces, and a synergistic effect between the crystal faces is improbable. Hence, the result that Ag particles were deposited on the {001} and {011} faces at high velocities does not simply mean that these faces are effective for reduction of Ag^+ ions. Instead, these faces are considered to be effective to carry out oxidation and reduction reactions at the same time.

Our results strongly suggest that the {110} face of rutile particles provides the effective reduction site and the {011} face works as the oxidation site. Because of such a synergistic effect between the {110} and {011} faces, rutile particles are considered to be very efficient for some kinds of photocatalytic reactions.

Different surface energy levels of the conduction and valence bands are expected for different crystal faces of TiO_2 because of the atomic arrangements characteristic of these faces.[24] The difference in the energy levels drives the electrons and holes to different crystal faces, leading to separation of electrons and holes. This separation is probably the key to the high efficiency of some photocatalytic reactions, such as water oxidation, which require band bending in TiO_2.[21] The effective separation of oxidation and reduction sites of rutile particles, as seen in Fig. 4(a), suggests that the electronic energy levels of the {110} face are lower than those of the {011} face. The difference is considered to be large enough to drive the photocatalytic oxidation of water on the rutile particles, when suitable electron acceptors are added to the solution. In the case of anatase particles, the effect of the crystal faces is small compared with the results obtained with rutile particles, probably because the difference in the energy levels between the crystal faces is small. This is probably why anatase particles have low activity for the oxidation of water, even when the particles are large. For oxidation of reactive compounds, such as alcohols, it is known that fine anatase particles are very active, especially when the concentration of the reactants is low.[25] In these reactions, it is considered that the effect of the crystal faces of the TiO_2 particles is small, because the band bending of TiO_2 is not necessary for these reactions.

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