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Formation of New Crystal Faces on TiO_2 Particles by Treatment with Aqueous HF Solution or Hot Sulfuric Acid

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We have demonstrated that new crystal faces are generated on anatase and rutile TiO_2 particles by means of chemical etching in aqueous hydrofluoric acid or hot sulfuric acid. By the treatment with aqueous hydrofluoric acid, the {112} face of anatase particles and the {021} face of rutile particles are newly formed. When treated with hot sulfuric acid, anatase particles exposed the {122} face, and rutile particles exposed the {001}, {010}, {021} and {121} faces. In both cases, anatase particles are etched at a higher rate than rutile particles. The etched particles are expected to show photocatalytic properties unique to the crystal faces. For example, the {112} face of anatase particles is demonstrated to be active for oxidation of Pb^{2+} ions.

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Semiconductor photocatalysts have attracted much attention because of their applicability to treatment of wastes and pollutants in air and water.[1-9] For these purposes, TiO_2 particles have been used most often because of their chemical stability and high activity. In some of these reactions, it has been found that crystal faces on TiO_2 particles play important roles.[10-12] The importance of crystal faces of photocatalyst particles should be related to the fact that oxidation and reduction occur simultaneously on each particle. The presence of different crystal faces on one particle is advantageous to providing oxidation and reduction sites on it owing to their different atomic arrangements.[13] It is also expected that the efficiency of electron-hole separation is enhanced due to the difference in the energy levels between different crystal faces. In the case of rutile TiO_2 particles, by using TiO_2 particles with developed crystal faces, we have demonstrated that the {110} face provides the reductive sites and the {011} face provides the oxidative sites.[11] However, the information about the effect of crystal faces has been limited, because the formation of developed crystal faces on TiO_2 particles is difficult. The chemical stability of TiO_2 is the drawback to developing crystal faces, although it is the great advantage for the purpose of photocatalysts.

Concerning the modification of the surface structure of rutile TiO_2, it has been known that certain crystal faces are selectively generated by the photoelectrochemical etching process in aqueous sulfuric acid.[14-16] However, such a process is not convenient to treat the surface of particles. A conventional chemical process which etches TiO_2 is immersion in concentrated sulfuric acid at high temperature. In addition, we recently found that aqueous HF solution etches TiO_2 particles, especially anatase particles.[17] Here, we report that each of these chemical treatments leads to new crystal faces on both rutile and anatase TiO_2 particles.

In order to observe the crystal faces formed on TiO_2 particle, we used a TiO_2 powder consisting of rutile (15%) and anatase (85%) particles.[11] The size of the rutile and anatase particles is both about 1 μm. The specific surface area of the powder was determined to be 1.1 m^2 g^{-1} by the BET method. Figure 1 shows the scanning electron microscope (SEM) images of the rutile and anatase particles included in the powder. The rutile particles expose the {110} and {011} faces, and the anatase particles mainly expose the {001} and {011} faces. The assignment of the crystal faces was reported previously.[11]

SEM images of the anatase TiO_2 particles after the treatment with 10% HF solution for 24 h are shown in Fig. 2. By comparing the structure with that before etching (Fig. 1 a), it is found that the side line of two {011} faces is selectively etched. As a result, 8 new faces are generated on each particle. The newly developed crystal face was assigned to the {112} face on the basis of the observed angels between this face and the other faces on a particle. More precisely, the observed angle with the {001} face agreed with the theoretical value of 119.4 degrees within an error of 3 degrees. The other new crystal faces shown below are also assigned in such a way. The relative size of the newly formed {112} faces on an anatase particle increases as the particle size decreases, as seen in Fig. 2. This result suggests that the {112} face grows at a constant rate irrespective of the original particle size.

In the case of rutile particles, the etching rate in 10% HF solution was very slow, and practically no etching was detected after the treatment for 24 h. After treatment for a week, we observed new {021} faces which are exposed at the vertex surrounded by two {110} faces and a {011} face, as shown in Fig. 3. The slow etching rate of rutile particles in aqueous HF solution has already been confirmed from the change of X-ray diffraction patterns of a TiO_2 powder consisting of rutile and anatase particles.[17]

In the study of photoelectrochemistry of TiO_2 electrodes, in order to remove the surface damages, rutile crystals are often treated with concentrated sulfuric acid at about 200-250 °C before the measurements.[18] We tried this treatment to the TiO_2 powder containing both anatase and rutile particles. Figure 4 shows the SEM images of anatase particles observed after this treatment for different time periods. The etching of the anatase particle starts from the intersection of a {001} face and two {011} faces. As a result, {122} and {212} faces are generated at the vertex. These faces are crystallographically identical because the anatase structure belongs to the tetragonal system. These crystal faces are seen after the treatment for only 1 min, as shown in Fig. 4 (a). These faces grow with the treatment time, and finally disk particles are formed, each of which is shaped by 16 planes of the {122} face, as seen in Fig. 4 (f) for 25 min etching.

The etching rate of rutile particles in hot sulfuric acid is slower than that of anatase particles. No change in the shape of rutile particles was detected after the treatment for 20 min. However, by continuing the treatment for 2 h, different kinds of new faces were developed on a particle. As seen in Fig. 5, they are assigned to the {001}, {010}, {021}, and {121} faces. The numbers of the {001}, {010}, {021}, and {121} faces appearing on a rutile particle are 2, 4, 8, and 16, respectively.

Concerning the effect of crystal faces of TiO_2 on the photocatalytic properties, we have reported that the {011} and {110} faces on rutile particles provide oxidative and reductive sites, respectively.[11] In the case of anatase particles, the {001} and {011} faces provide oxidative and reductive sites, respectively.[11] Such effects of the crystal faces were confirmed from the observation of the location of Pt and PbO_2 deposits, which are plated reductively and oxidatively, respectively, by photocatalytic reactions on TiO_2 particles without the etching treatment. By using the same experimental method, we have studied the effect of the newly developed crystal faces generated by the etching treatments.

Figure 6 shows a typical result obtained for anatase particles after treatment with 10% HF for 24 h. Small Pt deposits are seen mostly on the {011} faces after the photocatalytic oxidation of $PtCl_6^{2-}$ using 2-propanol as the sacrificial electron donor, as seen in Fig. 6 (a). On the other hand, larger PbO_2 deposits are seen on the {112} faces when Pb^{2+} was photocatalytically oxidized on the Pt-deposited TiO_2 particles, as shown in Fig. 6 (b). These results indicate that the {011} face provides the reductive sites and the {112} face provides the oxidative sites. The oxidative activity of the {112} face is considered to be stronger than that of the {001} face, which acts as the oxidative site on the TiO_2 particles before etching,[11] because no PbO_2 deposits are seen on the

{001} face of the etched particles, as shown in Fig. 6(b). This result suggests that the photocatalytic activity can be enhanced by the etching treatment. In the case of rutile particles, however, the deposits of Pt or PbO_2 are not seen on the faces newly generated by the etching treatment.

In summary, we have demonstrated that the surface structure of TiO_2 particles can be controlled by means of chemical etching methods. These etched TiO_2 particles are expected to show unique photocatalytic properties due to the new crystal faces.

Experimental

A 10% hydrogen fluoride solution was prepared by diluting 40% hydrogen fluoride (Morita Chemical Ind.) with deionized water. TiO_2 powder (2 g) was added to a Teflon beaker containing the 10% HF solution (100 ml), and the suspension was stirred for 24 h to 1 week at room temperature. After the treatment, the TiO_2 particles were separated by filtration and washed with deionized water. For the treatment of TiO_2 particles with sulfuric acid, concentrated sulfuric acid (Wako Chemicals) was used as obtained. For the etching with hot sulfuric acid, the TiO_2 powder (1.0 g) was added to a glass flask containing sulfuric acid (40 ml) at about 200 °C and kept standing for 1 min to 2 h. The etching was quenched by immersing the flask in cooled water, and the TiO_2 particles were filtrated and washed with deionized water.

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Figure captions

Figure 1. SEM images of anatase (a) and rutile (b) particles included in the TiO_2 powder used in this study.

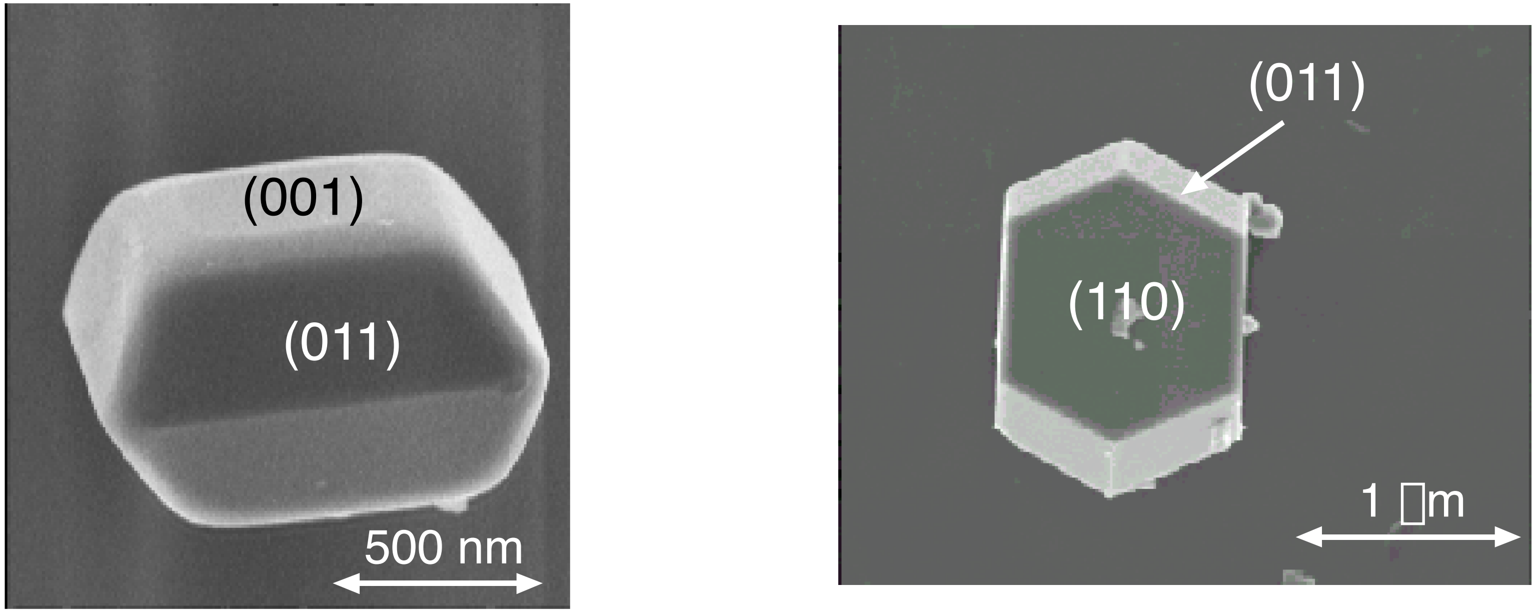
Figure 2. SEM images of anatase particles after treatment with aqueous 10% HF solution for 24 h. The sizes of the particles are about 1.8 nm (a), 1.4 nm (b) and 1.2 nm (c).

Figure 3. SEM image of a rutile particle treated with aqueous 10% HF solution for a week.

Figure 4. SEM images of anatase particles treated with hot sulfuric acid. The etching time periods are about 1 min (a), 5 min (b), 10 min (c), 15 min (d), 20 min (e) and 25 min (f).

Figure 5. SEM image of a rutile particle treated with hot sulfuric acid for 2 h.

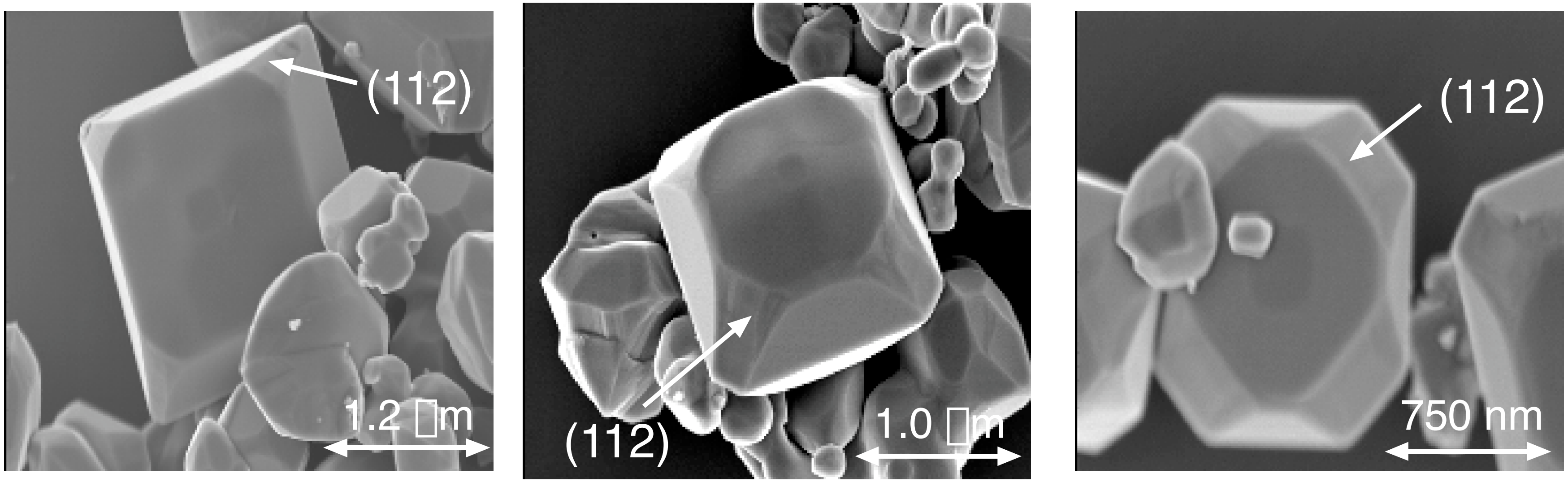
Figure 6. SEM images of an anatase particle after UV-irradiation in aqueous solution containing 1.0 mM H_2PtCl_6 and 0.52 M 2-propanol (a), and an anatase particle after sequential UV-irradiations in this solution and then in an aqueous solution of 0.1 M $Pb(NO_3)_2$ (b).



a

b

Fig. 1



a

b

c

Fig. 2

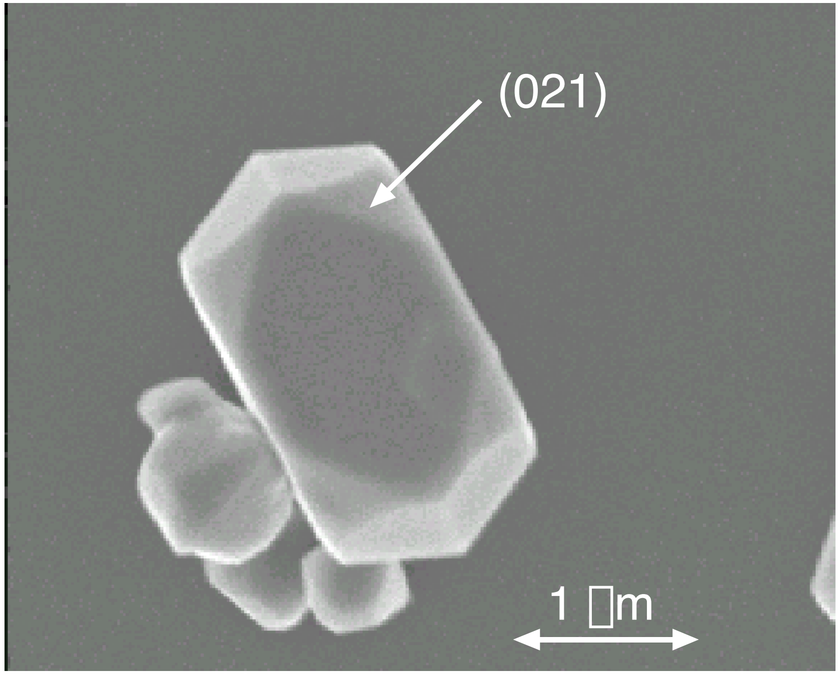


Fig. 3

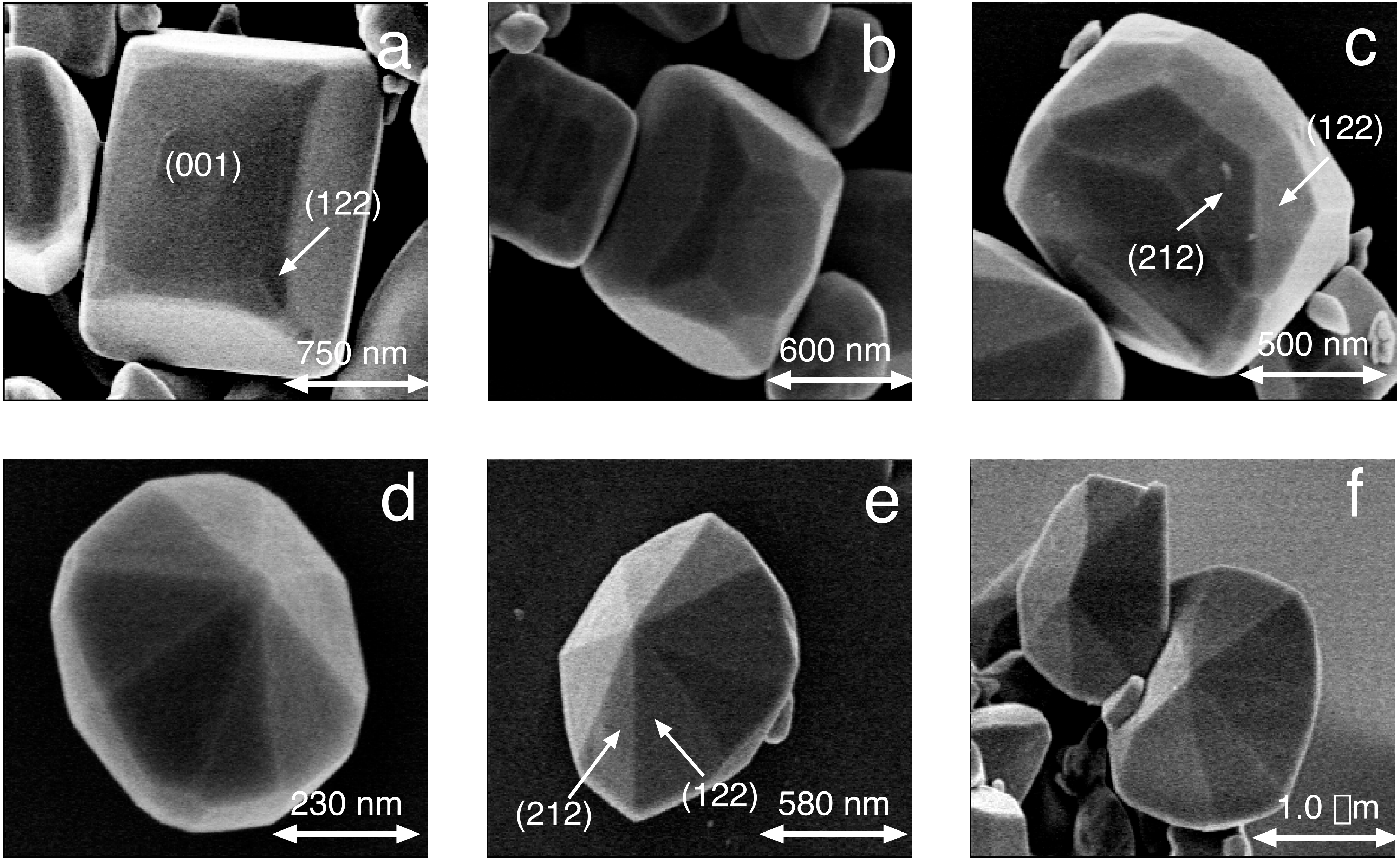

a
(001)
(122)
750 nm
b
600 nm
c
(122)
(212)
500 nm
d
230 nm
e
(212)
(122)
580 nm
f
1.0 m

Fig. 4

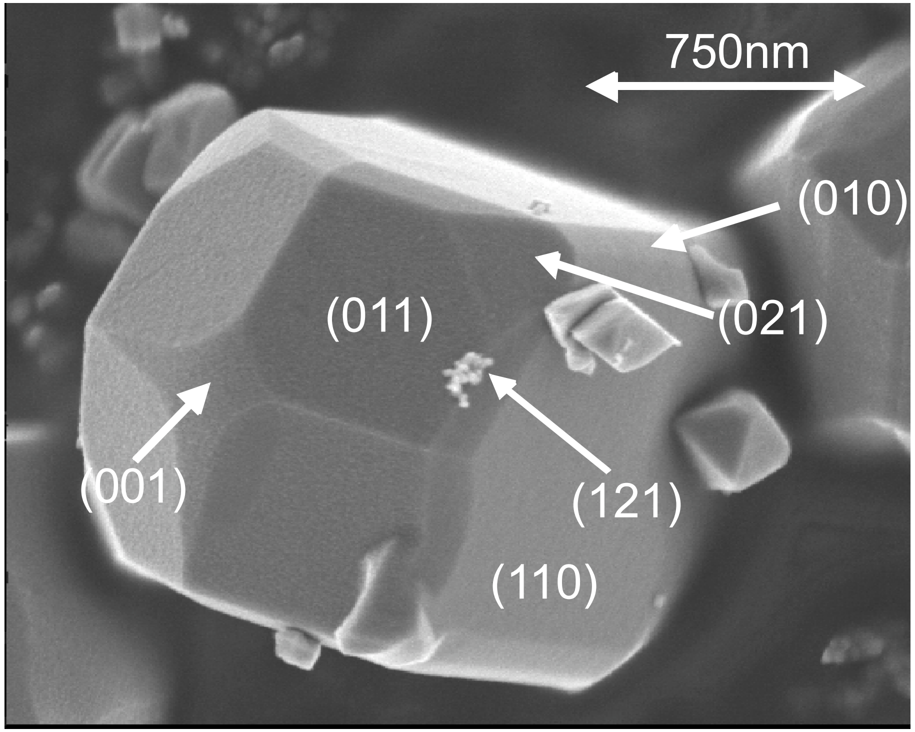
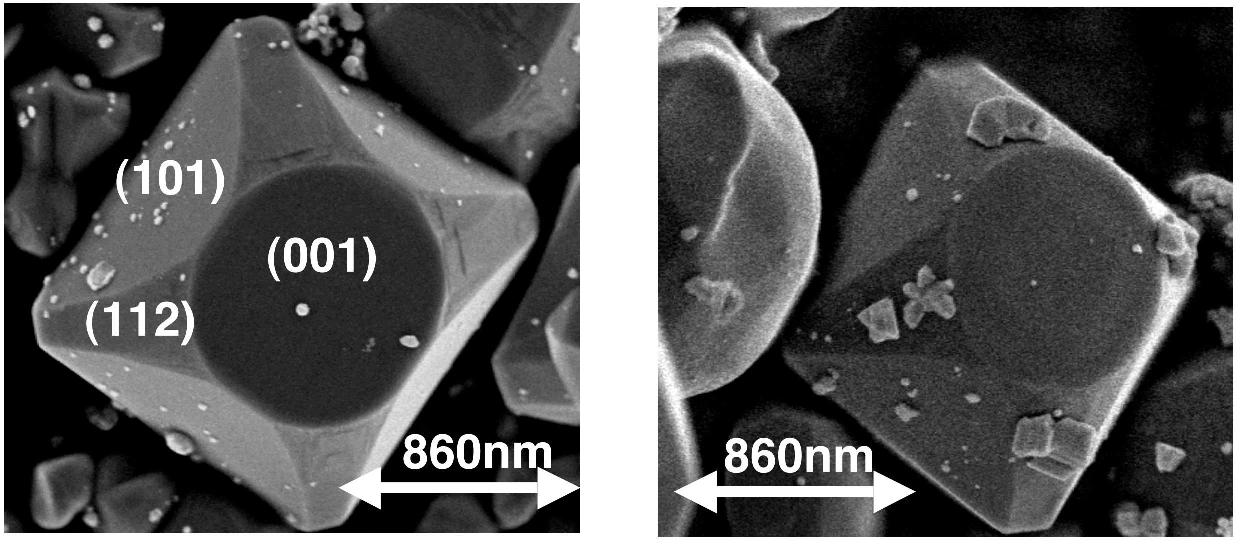


Fig. 5



(a) (b)

Fig. 6