

Change in Surface Properties across the Crystallographic Edge of Anatase TiO₂Kenichi OZAWA^{1,2,*}, Keita HIROMORI³, Nobuo NAKAJIMA³, and Kazuhiko MASE^{2,4}¹ Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan² Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan³ Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan⁴ SOKENDAI (The Graduate University for Advanced Studies), Tsukuba, Ibaraki 305-0801, Japan

1 Introduction

One of interesting properties that TiO₂ photocatalysts exhibit is that photocatalytic activity depends on the crystallographic orientation of the TiO₂ surfaces. Our recent X-ray photoelectron spectroscopy (XPS) studies [1, 2] has suggested that there is a strong correlation between photocatalytic activity and the photoexcited carrier lifetime on the TiO₂ surfaces. Another mechanism for the orientation dependent activity is proposed on the basis of discontinuity of the energy level alignment at the crystallographic edge where two surfaces with different orientation come in contact with each other. For example, the energy levels of the anatase TiO₂ has been proposed to lay deeper on the (101) surface than on the (001) surface so that the photoexcited electrons and holes tend to migrate to the (101) and (001) surfaces, respectively [3, 4]. However, such energy level discontinuity was only suggested by the work function, and a direct verification has not been done so far.

In the present study, using a high precision XYZ translator for manipulating the sample position [5], we examined the energy level alignment across the edge between the (101) and (001) surfaces of anatase TiO₂ by XPS. We also estimated the amounts of adsorbed acetic acid to compare the adsorption activity among the different surface sites.

2 Experimental

The XPS measurements were carried out at a beam line 13B of the Photon Factory [6], using an SES200 photoelectron energy analyzer (Gamma Data/Sienta). The photon energies of 400 eV and 753 eV were used to acquire the spectra. A naturally grown anatase TiO₂ single crystal with mirror-polished (101) and (001) surfaces which form a straight edge in between (SurfaceNet GmbH) was used (Fig. 1a). The (101) and (001) surfaces were cleaned by cycles of Ar⁺ sputtering and annealing at 950 K in 5 × 10⁻⁴ Pa O₂ atmosphere. A vapor of acetic acid was introduced to the loadlock chamber, in which the TiO₂ sample was stored to allow acetic acid to adsorb on the surfaces. The adsorption temperature was 300 K.

3 Results and Discussion

Fig. 1b shows a microscopic view of the surface morphology in the vicinity of the edge, obtained by adjusting the sample position while monitoring the Ti 2p_{3/2} photoemission image. The sample position was adjusted so as to lie the photoemission image on the microchannel

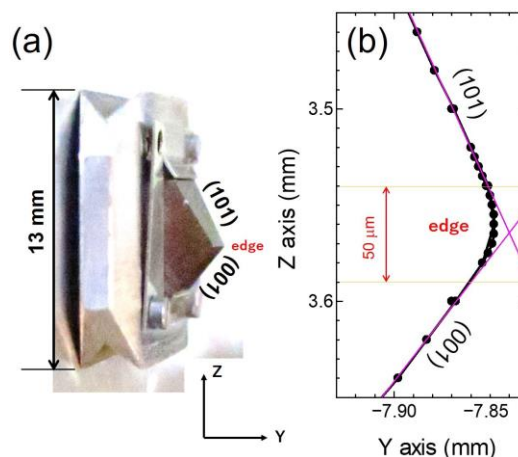


Fig. 1 (a) A natural crystal of anatase TiO₂ mounted on a molybdenum sample holder. (b) A line profile of the surface morphology around the (101)/(001) edge region. Circles indicate the positions of the TiO₂ surface, and straight lines indicate extrapolation of the (101) and (001) terraces.

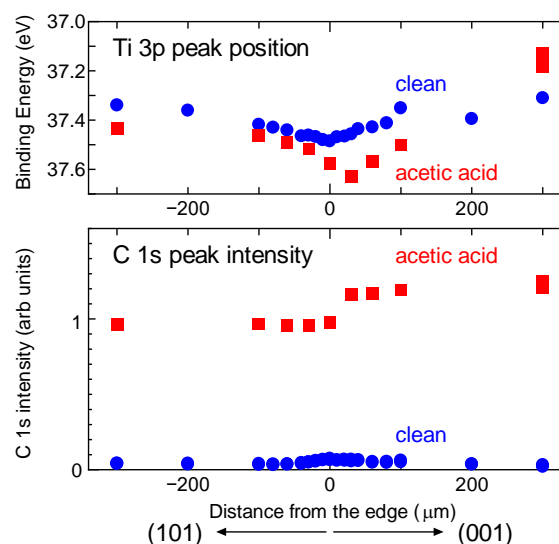


Fig. 2 Binding energies of the Ti 3p peaks (a) and integrated intensities of the C 1s peaks (b) of the clean and acetic-acid saturated TiO₂ surfaces as a function of the distance from the edge. Blue circles and red squares indicate the results of the clean and acetic-acid saturated surfaces, respectively.

plate (MCP) of the analyzer in the center position of the MCP. The edge is observed to be rounded with a width of ~ 50 μm . However, the size of the synchrotron radiation was ~ 30 μm in the vertical direction (the Z direction) [5], the edge should be sharper than that shown in Fig. 1b.

To evaluate the energy level alignment across the edge, peak positions of the Ti 3p spectra were determined. Fig. 2a shows that, on the clean TiO₂ surface, the binding energy of the Ti 3p peak is at 37.34–37.35 eV on both (101) and (001) terraces, while the peak position is 37.47 eV at the edge (blue circles). This suggests that the energy level of TiO₂ is nearly the same on both (101) and (001) terraces and is deeper by ~ 100 meV at the edge in between the two terraces. Namely, the TiO₂ band bends downwardly when going from the terraces to the edge, and the energy levels of the (101) and (001) are not smoothly connected at the edge. As the TiO₂ surface is being covered with acetic acid, a dip structure of the energy level is preserved, while the adsorption induces a slight downward band bending (squares in Fig. 2a).

Such a detailed band structure around the edge region has not been reported so far. The dynamic of the photoexcited carriers has been discussed on the basis of a simple and smooth energy level alignment at the edge between the (101) and (001) surfaces [3, 4]. Thus, it is needed to reconsider the carrier dynamics around the edge. The deeper lying of the TiO₂ level at the edge suggests an accumulation of the photoexcited electrons so that the photocatalytic oxidation reaction could be facilitated more at the edge than on the terraces.

Fig. 2b shows a variation of the C 1s peak intensity along the line from one terrace to the other terrace. Even after the extensive surface cleaning, carbon contaminants remain on the surface (blue circles). Despite the low concentration, a higher amount of the contaminants is found at the edge than on the terraces. This may reflect a higher number of coordinatively unsaturated atoms in the edge region.

As the surface is being covered with a saturation amount of acetic acid, the C 1s peak intensity is enhanced by more than 20 times (red squares in Fig. 2b). The amount of adsorbed acetic acid is higher on the (001) terrace than the (101) terrace. This means that the (001) surface of anatase TiO₂ is more active for acetic acid adsorption than the (101) surface. Interestingly, the edge, which is active for contaminants, is not an active site for acetic acid adsorption.

Although not shown here, the line profile of the Ti 2p/O 1s intensity ratio is found to be similar to the C 1s intensity profile; namely, the Ti 2p/O 1s ratio is higher on the (001) terrace than on the (101) terrace. This means that the surface Ti density is higher on (001) than on (101). Acetic acid is known to adsorb on the TiO₂ surfaces in the form of acetate, and each acetate is bonded to the surface Ti atom(s) via its O atom(s). Thus, the line profile of the C 1s intensity (the squares in Fig. 2b) can be understood by the proposed adsorption mechanism of acetic acid on the TiO₂ surface.

If the photoexcited carriers are drifted along the potential gradient (band bending), the electrons and the holes are assumed to be accumulated at the edge region and the terraces, respectively. Comparison of photocatalytic

activity among the edge and the (101) and (001) terraces is necessary to prove the carrier dynamics along the surface parallel direction in the vicinity of the crystallographic edge.

Acknowledgements

The XPS measurement was performed under the approval of the Photon Factory Advisory Committee (Proposal No. 2018S2-005). This work was financially supported by a Grant-in-Aid for Scientific Research (Grant No. 16H03867) from Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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