

Influence of atomic level surface local structure on photo-induced oxidation reaction of water at single crystal TiO₂ surface

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We previously reported that the oxygen photoevolution reaction on TiO₂ surface is initiated by a nucleophilic attack of an H₂O molecule to a surface-trapped hole (STH), accompanied by bond breaking. On this process, the trapped holes were also extinguished by the other 3 kinds of processes (PL emission by recombination with electrons, non-radiative recombination and surface roughening reaction (i.e. surface etching)) besides the oxygen evolution reaction [1]. It was expected that the above 4 kinds of reactions occurs at different surface sites and are correlative with each other. This indicates that those competitive reactions are strongly dependent on the surface local structure. We investigated how the surface local structure affects those competitive reactions on TiO₂ surface using atomically flat vicinal TiO₂(110) single crystal surface those step-terrace structure was strictly controlled.

Nb doped single-crystal vicinal TiO₂(110)(rutile) surfaces, tilted towards $\langle 001 \rangle$ and $\langle \bar{1}10 \rangle$ directions at angles of 0.5 and 2° were used as substrates. The illumination was carried out by use of a 365 nm band from a high-pressure mercury lamp. Fig 1 (a) shows the PL intensity vs. applied potential of TiO₂(110) surfaces tilting in $\langle \bar{1}10 \rangle$ direction at angles of 0.5 and 2°, those terrace width are 10 and 40 nm, respectively. The PL intensity took a maximum near the onset potential of photocurrent, indicating that the PL is arising from surface carrier recombination between conduction-band electrons and the surface-trapped holes. We can see that the PL intensity of the surface with 40nm terrace is larger than that of the surface with 10 nm terrace. Fig. 1(b) shows the PL intensity of the surface tilting in $\langle 001 \rangle$ and $\langle \bar{1}10 \rangle$ directions at an angle of 2°. The PL intensity of the surface tilting in $\langle \bar{1}10 \rangle$ direction was larger than that of the surface tilting in $\langle 001 \rangle$ direction. These results indicate that the PL intensity is strongly dependent on the terrace width and the step direction. The rate of the photo-induced etching reaction (surface roughening reaction) on each surface was also estimated. From those results, we revealed that the 2 kinds of competitive reactions (PL and surface roughening reactions) were strongly affected by the surface local structure of TiO₂ surface. These results strongly suggested that the oxidation evolution process (i.e. photocatalytic activity) is also affected by the local structure of the TiO₂ surface.

On the other hand, the surface roughening process induces the change of the surface local structure of TiO₂ (Fig. 2). Considering the fact that the surface local structure of photocatalyst affects the photocatalytic activity, it is quite possible that the photocatalytic reactivity of TiO₂ may be changed by the surface roughening process. We investigated the photocatalytic activity for oxygen photoevolution at the flat and roughened TiO₂ with a focus being placed on the behavior of the onset potential. The results indicated that there is a

large difference in the oxygen evolution efficiency between flat and roughened TiO₂ surface. By taking into consideration for the results of Mott-Schottky plot (flat band potential) and I-V curve measurements (onset potential and photocurrent density), it was revealed that such a difference in oxygen evolution efficiency was attributed to the difference in the activation energy of intermediates, induced by the difference of the surface local structure. Interestingly, it was also revealed that the consumption ratio of holes between the 4 kinds of competitive reactions was changed with the progress of the photooxidation reaction. Based on these results, the mechanisms of competitive reactions occurring on TiO₂ surfaces will be discussed.

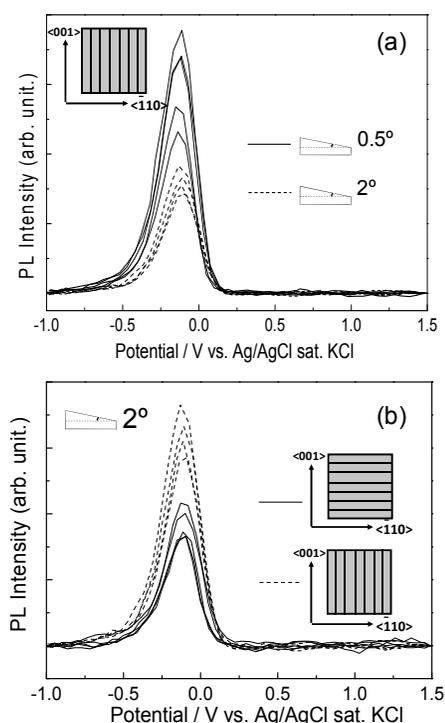


Fig.1 PL intensity vs. applied potential of vicinal TiO₂(110) surfaces

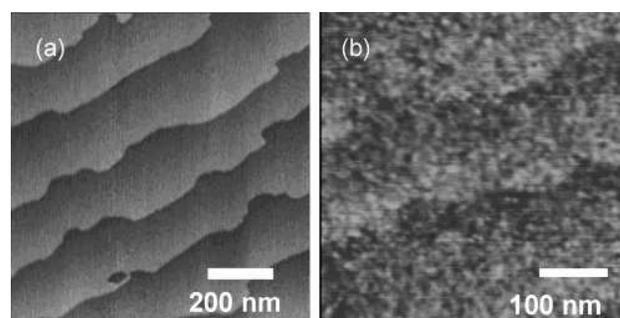


Fig. 2 AFM images of the atomically flat n-TiO₂(110) surface (a) before and (b) after the UV irradiation, during which the TiO₂ surface was immersed in (b) 0.1 M HClO₄ (pH 1.1).

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References:

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