OH radical Formation at Distinct Faces of Rutile TiO₂ Crystal in the Procedure of Photoelectrochemical Water Oxidation.

*Yukihiro Nakabayashi and Yoshio Nosaka*

Department of Materials Science and Technology, Nagaoka University of Technology,
Nagaoka, 940-2188 Japan

S1. AFM observation for TiO₂ single crystal electrodes

To evaluate the flatness of the surface of single crystal electrodes after using for photoelectrochemical water oxidation, AFM observation was carried out with Nano Navi (SII technology, Inc.) with DFM tapping mode (Scan frequency:1.00Hz, needle: SI-DF3R (100)). **Figure S1** shows AFM images for TiO₂ rutile single crystal electrodes. The symbols, (100), (110), and (001), indicate the orientation planes of single crystals. In the figure, (a), (b), and (c) are the top views, and (d), (e), and (f) are the cross sectional images taken along black lines in (a), (b), and (c), respectively. Clear contrasts appear in (a), (b), and (c) and they correspond to the height of the structures on the TiO₂ rutile single crystals. The flatness was examined by the slope of local structure, which
was calculated for the area indicated by yellow rectangle in (d), (e) and (f). The angles of surface slope are shown in each figure. Since the angle of the surface slopes were few degree, the surface of the electrodes is probably dominated in the crystal structure of each facet. The angles are so slight that we could judge it to be nearly flat to the orientation planes of the TiO$_2$ rutile single crystals. In the present experiments, since the single crystals were heat treated at 700 ℃ to acquire better conductivity, the crystalline surface may be roughened to a certain extent. However, the appearance of the surface dependence indicates that the majority part of the surface structure held the crystal structure even after the photo oxidation of water. Although Nakamura et al.\textsuperscript{1} reported the surface roughening after the oxidation, they used acidic solution 0.1M HClO$_4$ (pH 1.0) but in the present study we used 0.1M Na$_2$SO$_4$ (pH 6) as the electrolyte.

Figure S1 AFM images for the surface of TiO$_2$ rutile single crystal electrodes.

Figure S2. Calibration for the umbelliferone concentration from fluorescence spectra.

In 0.1 M Na$_2$SO$_4$ solution, the concentration of coumarin was fixed at 0.1 mM while the concentration of umbelliferone was varied from 0 to 20 nM. Excitation wavelength was 332 nm.
Figure S3  Cyclic voltammogram of the (100) and (110) electrodes

**Figure S3** Current-voltage curve of the TiO$_2$ rutile (a) (100) and (b) (110) electrodes in 0.1M Na$_2$SO$_4$ solution under UV irradiation (red curve) and dark condition (blue curve). Scan rate was 50 mV/s.

Figure S3 shows CV curves for the (100) and (110) electrodes under dark and UV light irradiation. For these two electrodes, the CV curves under the UV irradiation showed small deviation due to the O$_2$ bubble formation by an insufficient stirring at that time. In order to measure the O$_2$ concentration, we assembled a special cell for electrolysis by using three necked round bottom flask, where an ion exchange membrane to separate the TiO$_2$ electrode and the Pt counter electrode was inserted. Therefore, the resistance of ion conductivity between the two electrodes became large. As a result, the current still increased even at the 2 V vs. Ag/AgCl.