

Efficient Water Photooxidation at the (100) Face of n-TiO₂ (Rutile) Exposed by Photoetching

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The elucidation of molecular mechanism of water photooxidation on n-TiO₂ is important for finding new active electrode materials for water electrolysis as well as improvement in the photocatalytic activity. Studies with well-defined TiO₂ surfaces on an atomic scale are of key importance to get a definite conclusion.

In previous papers (1,2), we reported that rectangular nano-holes or grooves with the (100) face, extending in the <001> direction, were selectively formed by photoetching of n-TiO₂ (rutile) in 0.05 M H₂SO₄ (see Fig. 1), which occurred slightly and competitively with water photooxidation. A similar result was reported recently by Minoura et al. (3). The result enabled us to investigate the crystal-face dependence of the water photooxidation activity. In the present paper, we report that the water photooxidation proceeds most efficiently on the photoetched, (100)-exposed n-TiO₂ (rutile) electrode, in particular under weak illumination. The high efficiency can be explained by taking account of the specific atomic structure of the (100) face including the presence of atomic grooves (Fig. 2), which can trap photogenerated holes effectively.

Fig. 3(A) shows a photocurrent (j) vs. potential (U) curve for the photoetched, (100)-exposed n-TiO₂ (see Fig. 1) compared with that for non-photoetched n-TiO₂, under weak illumination. The onset potential of photocurrent for the former electrode is about 0.1-0.2 V more negative than that for the latter, indicating that the former is more active for the water photo-oxidation than the latter, under weak illumination. Under strong illumination, almost no difference was observed (Fig. 3B).

The above result was confirmed by measurements of the photoetching quantum efficiency (η_{pe}) (Fig. 4). The η_{pe} for the photoetched, (100)-exposed n-TiO₂ (001) was much lower than that for the non-photoetched n-TiO₂ in a region of weak illumination (small saturated photocurrent densities), again indicating that the former electrode is more active for the water photo-oxidation (competing with the photoetching) than the latter, under weak illumination.

The crystal-face dependence of the water photo-oxidation activity cannot be explained by assuming the conventional scheme of direct oxidation of surface OH by photogenerated holes, because surface OH is present in all the TiO₂ surfaces. The result can be explained by taking account of the presence of atomic grooves at the (100) face (Fig. 2), which can trap photogenerated holes effectively. The water oxidation will be initiated by nucleophilic attack of H₂O to the holes, resulting in the Ti-O bond breaking and formation of Ti-O· radicals, followed by their coupling leading to formation of surface peroxide. The model can explain the other experimental results such as the selective exposition of the (100) face by photoetching and the illumination intensity dependence of the intensity of the PL band arising from a surface reaction intermediate.

1) Y. Nakato, H. Akanuma, J. -I. Shimizu, Y. Magari, *J. Electroanal. Chem.*, **396**, 35 (1995).

2) A. Tsujiko, K. Kisumi, Y. Magari, K. Murakoshi, Y. Nakato, *J. Phys. Chem. B* **104**, 4873 (2000).

3) T. Sugiura, T. Yoshida, and H. Minoura, *Electrochem. Solid-State Lett.*, **1**, 175 (1998).

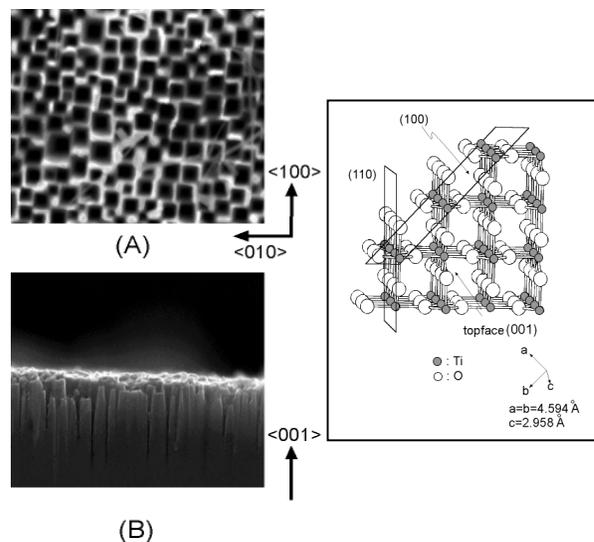


Fig. 1 SEM of photoetched n-TiO₂ (001) (A: top surface, B: cross section). Fig. 2 Crystal structure model for rutile TiO₂

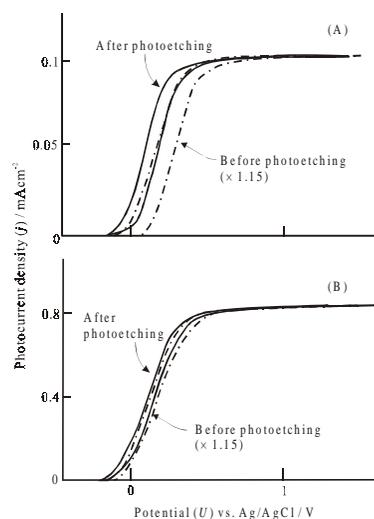


Fig. 3 The j - U curves for the photoetched, (100)-exposed n-TiO₂ (001) electrode compared with that for non-photoetched n-TiO₂ in 0.05 M H₂SO₄, under (A) low and (B) high illumination intensities.

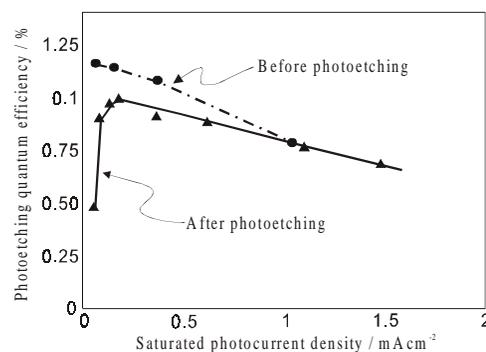


Fig. 4 The photoetching quantum efficiency (η_{pe}) for the photoetched, (100)-exposed n-TiO₂ (001) electrode in 0.05 M H₂SO₄, compared with that for non-photo-etched n-TiO₂, as a function of the illumination intensity (i.e., saturated photocurrent density).