

Titanium dioxide (TiO₂) is widely used as a photocatalyst. Its surface treatments such as control of surface atomic arrangement and surface modification are important not only to control catalytic reactions on TiO₂ surfaces, but also to enhance functionalities and properties. One of the most studied modifiers is organic molecules with terminal carboxyl groups. In order to expand the range of modifiers, it is essential to use molecules terminated with nitrogen-containing groups other than those terminated with carboxyl one. There are two methods to modify the TiO₂ surface, such as vacuum deposition and solution immersion, however, there are few studies on the interaction between nitrogen-containing molecules and the TiO₂ surface prepared by the solution immersion method. Because the adsorption behaviors in the solution are different from those in vacuum and because the former is easier and cheaper than the latter, it is important to investigate the effects of nitrogen-containing organic molecules on the TiO₂(110) single-crystal surface, which is the most thermodynamically stable and often used as a model surface, in the former.

This thesis consists of 6 chapters. In Chapter 1, as an introduction, photocatalytic reaction of TiO₂, and the surface structure and surface treatment method of rutile TiO₂(110) single-crystal surface were reviewed. In addition, the purpose of this thesis was described in Chap. 1.

In Chapter 2, the fundamentals and principles of the experimental methods used in this thesis were described, such as atomic force microscopy, AFM, X-ray photoelectron spectroscopy, XPS, and contact angle measurement, CAM. In addition, the data analysis methods were also described in Chap. 2.

In Chapter 3, aniline (AN) was selected as a representative example of a nitrogen-containing organic molecule, and the effect of AN on the TiO₂(110) surface was investigated.¹⁾ It is known that AN is uniformly modified on the TiO₂(110) surface when it was vacuum deposited. However, AN was not modified on the TiO₂(110) surface from the solution. Nevertheless, its surface morphology were significantly different before and after the immersion into the ethanol solution containing AN (Fig. 1).

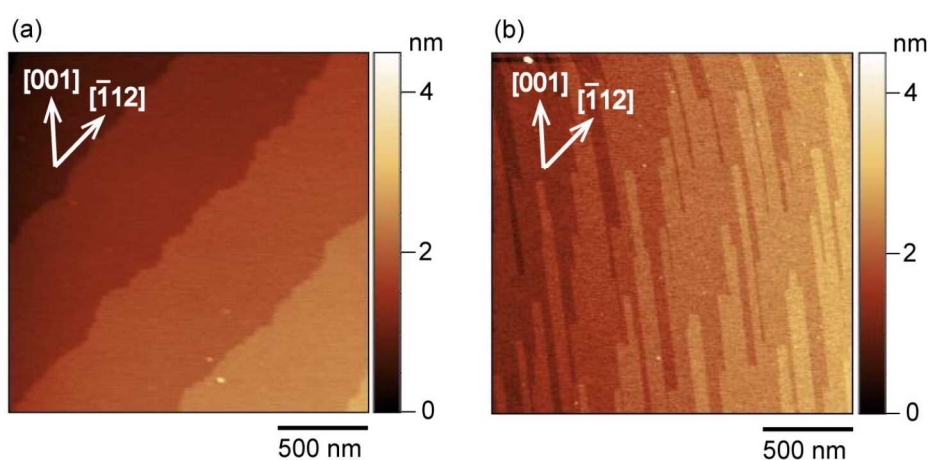


Figure 1 AFM images of (a) Et(24h) and (b) AN10(24h) (2 $\mu\text{m} \times 2 \mu\text{m}$)¹⁾.

Zigzag steps in the $[\bar{1}12]$ direction with many kinks were observed in the sample prepared by immersion into the solution without AN (Et(24h)), whereas linear $[001]$ direction steps were observed when the sample was immersed in the solution containing AN (AN10(24h)). Since Ti was detected in the solution after immersion, it was concluded that the etching was promoted by the formation of TiO_2 -AN complex and its desorption as a result of adsorption of AN to step edged Ti, as shown in Figure 2.

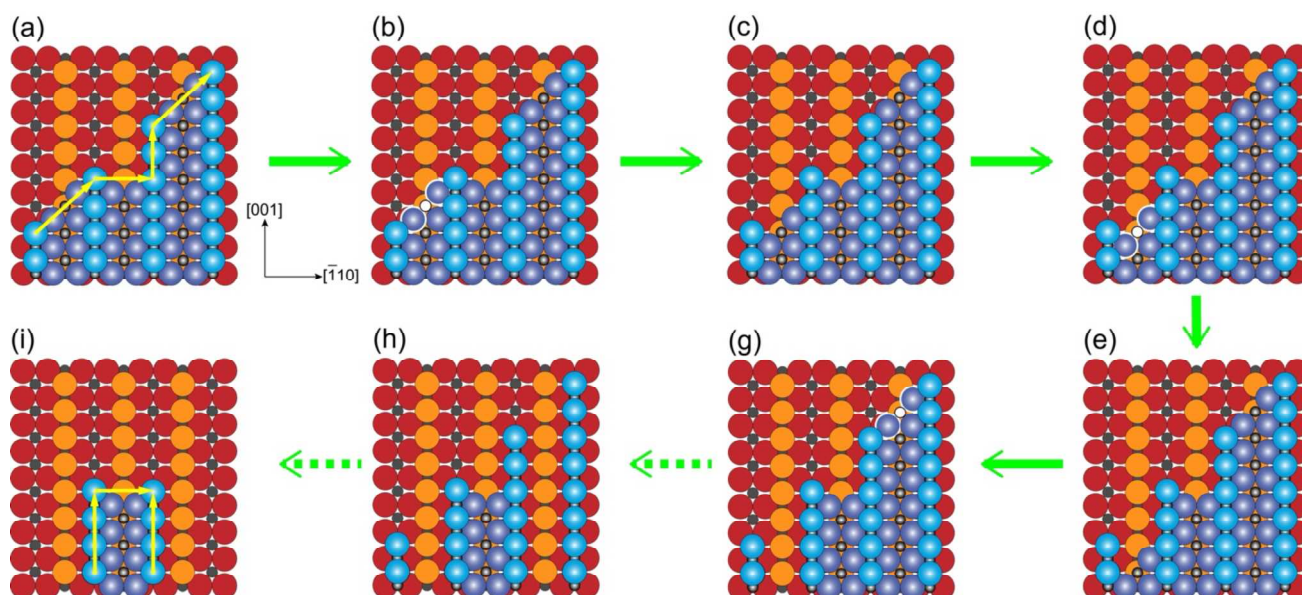


Figure 2 Schematic illustration of the formation process of atomically linear $[001]$ directional steps from zigzag $[\bar{1}12]$ directional steps on the $\text{TiO}_2(110)$ surface ¹⁾.

In Chapter 4, *N*-methylaniline (MAN) and pyridine (PY) were employed as new nitrogen-containing organic molecules and their effects on the $\text{TiO}_2(110)$ surface were investigated. By comparing with AN, it was concluded that the sequence of etching degree was $\text{AN} > \text{MAN} > \text{PY}$. It is considered that this tendency was due to the degree of steric hindrance around N.

In Chapter 5, the modification behaviors of nitrogen-containing organic molecules with carboxyl group, aminobenzene carboxylic acid (ABA) and (methylamino)benzene carboxylic acid (MABA), onto the $\text{TiO}_2(110)$ surface were investigated. When ABA and MABA were compared with BA, which modifies to saturation in a monomolecular layer, it was found that ABA and MABA modify even more, due to interaction between molecules. The etching effects were also observed for ABA and MABA, indicating the possibility of the step direction control with the molecular modification.

Finally in Chapter 6, this thesis was summarized.

Reference

1) M. Takahari, T. Goto, S. Yoshimoto, T. Kondo, *Chem. Lett.*, 52 (2023) 823. doi: 10.1246/cl.230334