Structural Change of the Rutile-TiO$_2$(110) Surface during the Water Wettability Transition Studied by X-Ray CTR Scattering

A hydrophobic TiO$_2$ surface can be converted to a hydrophilic one by UV light irradiation. This phenomenon was discovered about 20 years ago and has been used in coating applications. However, the mechanism is not well understood. In particular, it is not clear whether and how the surface structure is involved. We studied the possible structural change of the rutile-TiO$_2$(110) surface by using X-ray crystal truncation rod (CTR) scattering. We observed the occurrence of the surface structural change in real time during the photoirradiation. We determined the structure of hydrophobic and hydrophilic surfaces and propose a possible mechanism of the water wettability transition.

TiO$_2$ is a major photocatalyst used in a wide range of applications. In the late 1990s, it was found that a hydrophobic TiO$_2$ surface can be converted to a hydrophilic one by irradiating it with UV-light whose energy is greater than the bandgap of 3 eV [1]. This photoinduced property extends the range of applications to, for instance, anti-fog coatings, self-cleaning coatings, and heat dissipation coatings [2]. However, the mechanism of the wettability transition remains unclear, even though many experimental and theoretical studies have attempted to determine the atomic-scale processes occurring at the surface. In particular, there is no consensus about whether the surface structure changes during the wettability transition. Several groups concluded that photocatalytic decomposition of hydrophobic surface contaminants results in the hydrophilic surface [3]. In contrast, other groups claimed that an intrinsic photoinduced surface structural change leads to the hydrophilicity [4]. The controversy likely arises from the difficulty in observing the possible surface structural change at the atomic scale under ambient conditions, as conventional electron-based surface science techniques generally cannot be used under such conditions. Furthermore, since the hydrophilic surface is a short-lived metastable state in vacuum, *in-vacuo* surface analysis is difficult [2]. Theoretical studies are also challenging, since the energy hierarchy of the water adsorption phases is affected by the calculation conditions [5]. X-ray crystal truncation rod (CTR) scattering is capable of determining atomic structures across interfaces under ambient conditions. Thus, an *in-situ* CTR study can provide valuable information on the surface structural change.

We performed time-resolved and static CTR scattering measurements on the rutile-TiO$_2$(110) surface under humid conditions [6]. The surface structural change was observed in real time by using the wavelength-dispersive method (**Fig. 1a**) [7]. The time-resolved measurements were performed at AR-NW2A. We observed the change of scattering profile of the (01L) rod during UV-light (λ = 365 nm, 87 mW/cm^2) irradiation (**Fig. 1b**). **Figure 1c** shows the time evolution of the intensity at the

Figure 2: Structural models of the **(a)** hydrophobic and **(b)** hydrophilic surfaces. Hydrogen bonds are represented by light-blue lines.

different positions of the (01L) rod, which clearly shows that the intensity change is not uniform along the rod, namely, the intensity increases at L = 1.32, decreases at L = 1.85, and hardly changes at L = 1.65. Such a non-uniform change demonstrates the occurrence of an atomic-scale structural change. The changes in intensity almost finish in a few hundreds of seconds; this timescale is consistent with that of the wettability transition as observed by water contact angle measurements [4].

Details of the surface structural change were revealed by quantitative structure analysis of static CTR data measured on the hydrophobic (non-photoirradiated) and hydrophilic (photoirradiated) surfaces [6]. The measurements were performed at BL-4C. Based on the structure analysis, the following structure model is suggested for the hydrophobic surface. The surface TiO layer is terminated with two kinds of oxygen atoms, denoted by O$_T$ and O$_B$ in **Fig. 2a**. The determined Ti–O bond length indicates that the O$_T$ is in the form of a water molecule and the O$_B$ is not bonded with hydrogen atoms. The surface is partially covered with ordered water molecules (denoted by AW). On the hydrophilic surface, the analysis indicates that large positional fluctuations occur at the O$_T$, O$_B$ and the surface TiO layer and that the ordered AW layer becomes disordered.

The structural change can be interpreted, in terms of the water wettability transition, as being caused by a photoinduced proton transfer from the intact water at the O$_T$ site to the non-hydroxylated oxygen at the O$_B$ site, which results in an increase of population of the surface OH group. It is known that the photo-generated hole and electron finally reach the surface. According to ref. 8, the intact water at the O$_T$ site reacts with the hole to become an OH group, and the proton emitted from the water can be transferred to the neighboring non-hydroxylated oxygen at the O$_B$ site. The resulting OH groups

at the O$_T$ and O$_B$ sites can be active sites for the water adsorption, and a larger number of water molecules can be adsorbed (**Fig. 2b**). The OH groups at the neighboring O$_T$ and O$_B$ sites can make a hydrogen bond with each other. The hydrogen bonds might cause a large positional displacement of the O$_T$ and O$_B$ from the lattice site, which can induce local lattice strain at the underlying TiO layer, as observed in the CTR analysis. The adsorbed water molecules on the relatively disordered surface might be so disordered that they are invisible in the diffraction data analysis. The relatively disordered surface would be metastable and would recover to the hydrophobic one in the dark [2].

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Figure 1: (a) A schematic illustration of the time-resolved CTR measurement in wavelength-dispersive mode during UV-light irradiation on the rutile-TiO$_2$(110) surface. **(b)** Scattering intensity profiles of the (01L) rod measured at the photoirradiation (λ = 365 nm, 87 mW/cm^2) time of 10 s and 400 s. **(c)** Time evolutions of the normalized intensity at selected points (indicated by arrows in **(a)**) of the (01L) rod.