A Surface Science Approach to Unveiling the TiO₂ Photocatalytic Mechanism: Correlation between Photocatalytic Activity and Carrier Lifetime

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Establishing an accurate view of the photocatalytic mechanism of titanium dioxide (TiO₂) has been a challenging task since the discovery of the Honda-Fujishima effect. Despite the great success of catalytic studies in elucidating the chemical and physical aspects of photocatalysis, many questions remain. A surface science approach, which is characterized by the use of atomically well-defined surfaces in precisely controlled environments, is a powerful tool to shed light on the fundamental mechanism, especially the dynamics of photoexcited carriers. In the present contribution, recent progress in photocatalytic research that correlates photocatalytic activity and carrier dynamics on rutile and anatase TiO₂ is reviewed. A special focus is placed on the lifetime of photoexcited carriers. We present a method to determine the carrier lifetime; pump-probe time-resolved soft X-ray photoelectron spectroscopy, utilizing an ultraviolet laser as a pump light and a synchrotron radiation as a probe light. The carrier lifetime is found to be linearly correlated with the photocatalytic decomposition/desorption rate of acetic acid adsorbed on single-crystal TiO₂ surfaces. The important role of a potential barrier on the TiO₂ surface, which influences the carrier lifetime and the photocatalytic activity, is discussed.

Keywords Photocatalysis; Carrier lifetime; Photoelectron spectroscopy; Synchrotron radiation; Time-resolved measurement
I. INTRODUCTION

The outstanding photocatalytic activity of titanium dioxide (TiO₂) has attracted considerable attention since the discovery of electrochemical photolysis of water at a TiO₂ electrode by Honda and Fujishima in the late 1960s [1, 2]. TiO₂ photocatalysis is not limited to the photolysis of water [1–3]; novel phenomena such as the oxidation of cyanide ions in aqueous solutions [4], decomposition of carbohydrate into H₂ and CO₂ [5], removal of dilute nitrogen oxides (NOₓ) in air [6], inactivation of E. coli [7], etc. were also reported in the 70s, 80s, and 90s. These properties paved the way for the use of TiO₂ in environmental cleanup applications (air and water purification). Furthermore, the discovery of superhydrophilicity on the TiO₂ surface by ultraviolet (UV) illumination in 1997 [8] has led to applications such as self-cleaning tiles and anti-fogging mirrors, whose surfaces are coated by TiO₂ thin films. The global market for photocatalysis applications has grown steadily over the past decades [9] and is expected to keep expanding in the coming decades.

II. BRIEF OVERVIEW OF PHOTO-CATALYTIC ACTIVITY

A. Role of photogenerated carriers

In TiO₂ photocatalysis, a key factor is, evidently, photogenerated electrons and holes (Figure 1). Although a fraction of these carriers is lost by electron-hole recombination before they reach the catalyst surface, surviving electrons and holes initiate reduction and oxidation reactions, respectively, at the surface. In the case of photocatalytic water dissociation, two electrons and two holes are involved in the dissociation of a H₂O molecule [2]:

\[ \text{H}_2\text{O} + 2\text{h}^+ \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ \]

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]

The photocatalytic decomposition of organic compounds is more complex. Firstly, electrons and holes are considered to generate reactive oxygen species (ROSs) in the following manner [10, 11):

\[ \text{e}^- + \text{O}_2 \rightarrow \text{O}_2^- \]

\[ \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \]

\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \]

\[ \text{h}^+ + \text{O}_2^- \rightarrow 2\cdot\text{O}^- \]

Here, \( \cdot\text{OH} \), \( \cdot\text{O}^- \), and \( \cdot\text{O} \) are ROSs that interact with organic compounds; this constitutes the initial step of a series of chain reactions that lead to the total decomposition of compounds into CO₂ and H₂O.

Because of the essential role of photogenerated carriers, it is indispensable to focus on the dynamics of these carriers. Laser-assisted time-resolved measurement techniques are very powerful for the elucidation of the carrier dynamics in the femtosecond to microsecond time domains. Figure 2 summarizes the carrier dynamics in each time domain [11, 12]. Photogenerated electrons and holes are loosely bound by Coulomb forces, forming excitons. A large portion of the excitons undergoes immediate recombination after photogeneration, within femtoseconds. A remaining portion dissociates into free electrons and holes. In the TiO₂ crystals, there are many carrier traps: “shallow traps” and “deep traps”. The former is related to O defects, and the latter to unsaturated Ti atoms [13]. A part of migrated carriers is captured by these traps within femtoseconds to picoseconds after photogeneration, and the trap-mediated recombination process follows in picoseconds to nanoseconds. It is noted that electron-hole recombination via band-to-band transition occurs when the trap density is sufficiently low. Surviving free carriers reach the catalyst surface within nanoseconds to microseconds after photogeneration, and the transfer to adsorbates (adsorbed O₂, for example) occurs in tens to hundreds of microseconds. It is estimated that photoexcited carriers that are utilized in photocatalytic reactions represent only 10% of all photoexcited carriers; the rest is quenched by electron-hole recombination [11, 12, 14].

B. Carrier lifetime measurements

It is well known that the photocatalytic activity is higher for anatase TiO₂ than rutile TiO₂ [15–20]. One of the earliest studies that reported this phenomenon was by Tanaka et al. in 1991 [15]. They compared the initial degradation rates of organic compounds (C₂HCl₂, CH₂CICOOH, and phenol) in aqueous solutions using commercially available TiO₂ samples under illumination of a filtered mercury light and found that the TiO₂ samples with a higher anatase content exhibited higher degradation rates. The authors proposed that the higher activity resulted from a lower concentration of surface OH species, i.e., the consumption of ROS via \( \text{O}_2^- + \cdot\text{O} \) was suppressed on the anatase surface [15].
On the other hand, a more preferred explanation for the structural dependence of the photocatalytic activity nowadays is the difference in photogenerated carrier lifetime. Photoexcited carriers in a bulk material is believed to have a longer lifetime in anatase TiO$_2$ than rutile TiO$_2$, reflecting a difference in the band-gap type of bulk crystals, i.e., a direct band gap for rutile TiO$_2$ and an indirect band gap for anatase TiO$_2$ [21]. Xu et al. experimentally demonstrated that the reaction rates of CO oxidation on anatase TiO$_2$(101) and rutile TiO$_2$(110) were correlated with the bulk carrier lifetimes [19]. Moreover, Luttrell et al. proposed that the carrier transport from the bulk to the surface should also be taken into account when studying the photocatalytic activity [20]. Therefore, it is logical to expect that the carrier lifetime as well as its dynamics determine the photocatalytic activity of TiO$_2$.

However, the situation is not as simple as one may expect. Table 1 shows carrier lifetimes of TiO$_2$ measured by various time-resolved techniques, reported in several studies [22–28]. The values range from picoseconds to microseconds, irrespective of the crystal structure. It is obvious that factors other than the crystal structure affect the carrier lifetime. The morphology of the TiO$_2$ catalyst (nanoparticles or single crystals) and the environment surrounding the catalysts (solution, air, or vacuum) are possible influential factors. Nevertheless, it is difficult to comprehensively interpret experimental data and to predict the trend of the carrier lifetime based on these data.

C. Surface potential barrier

TiO$_2$ is an n-type wide band-gap semiconductor with a band-gap energy of approximately 3 eV (2.9–3.0 eV for rutile and 3.1–3.2 eV for anatase [29]). When the charge balance between the crystal surface and the bulk is disrupted, band bending is induced [Figure 3(a–c)]. For both anatase and rutile TiO$_2$ surfaces, when oxygen vacancies (V$_O$) are formed, downward band bending is induced and a charge accumulation layer is formed because V$_O$ acts as an electron donor [Figure 3(c)]. Such surfaces are easily obtained, as demonstrated in Figure 3(d), which shows a series of X-ray photoelectron spectroscopy (XPS) profiles in the valence-band region of rutile TiO$_2$(110) surface. The sample was prepared by Ar$^+$ sputtering and annealing at 650 K in an ultrahigh vacuum (UHV). The photon energy ($h\nu$) dependence of the valence-band maximum (VBM) position, which moves from 3.14 eV ($h\nu = 1465$ eV) to 3.37 eV ($h\nu = 100$ eV), is suggestive of downward band bending, because the detection depth increases with increasing excitation energy, according to the inelastic-mean-free path of the emitted photoelectrons [30] and the definition of information depth [31].

However, downward band bending is partially or completely suppressed when the TiO$_2$ surfaces are exposed to
gases such as CO and O₂ [Figure 3(e)]. These molecules are adsorbed on the V O sites and withdraw donated electrons from the accumulation layer. O₂ is more effective than CO because of its stronger electron-withdrawing ability. H₂O, which is adsorbed dissociatively on the TiO₂ surfaces, on the other hand, shifts the VBM to higher binding energies [32].

Since TiO₂ photocatalysts usually function in air or in aqueous solutions, O₂ and H₂O cover the TiO₂ surface. Thus, the type of the space charge region (SCR), i.e., a depletion type or an accumulation type, on the working photocatalysts depends on the adsorbed molecules and their coverages.

Considering the role of the photoexcited carriers (electrons and holes), the importance of the surface band structure must be recognized because the carrier dynamics is strongly affected by the SCR. The SCR acts as a potential

**Table 1:** Experimentally determined lifetimes of photoexcited carriers in TiO₂ photocatalysts along with crystal structures, form, particle size, measurement techniques, and surrounding environments.

| Structure  | Form       | Particle size | Lifetime  | Technique        | Environment | Refs. |
|------------|------------|---------------|-----------|------------------|-------------|-------|
| anatase a  | particle   | 2 nm          | 23 ps     | transient absorption | solution    | [22]  |
| anatase    | particle   | 2.4 nm        | 75 ps     | transient absorption | solution    | [23]  |
| anatase    | particle   | 21 nm, 400 nm | 1 ps      | transient absorption | air         | [24]  |
| rutile     | particle   | 30–50 nm, 640 nm | several hundreds of ps | 10 ns |
| anatase    | single crystal |           | 1–4.6 μs, 11–33 μs | photoluminescence | air         | [25]  |
| anatase    | single crystal |           | 15 ps (12 K), 150 ps (RT), 600 ps (12 K) | photoluminescence | vacuum     | [26]  |
| anatase    | particle   | 24–127 nm     | 150 ps–1 μs | photoluminescence | solution    | [27]  |
| anatase    | single crystal |           | 31 ns, 350 ns (e⁻) b | transient absorption | air         | [28]  |
| rutile     | single crystal |           | 24 ns (e⁻) b, 48 ns (h⁺) b | photoluminescence | photoconductivity |

a Crystal structure of the TiO₂ nanoparticles is not mentioned [22] but is speculated from the particle size and thermodynamic stability.
b Electron and hole lifetimes were separately evaluated [28].

**Figure 3:** (a−c) Energy level diagrams of three types of n-type semiconductor surfaces: (a) flat band, (b) upward band bending, and (c) downward bending. A space charge region is where the electronic band is bent. Schematic of the free-charge distribution is shown in the lower part of each panel. (d) XPS profiles of rutile TiO₂(110) in the valence-band region measured with different hν. The inset shows XPS profiles in the whole valence-band region. Spectral intensities are normalized by photocurrents of a final-stage focusing mirror. A shift of the VBM as a function of hν suggests downward band bending on this surface. (e) Near-ambient pressure XPS (NAP-XPS) profiles of rutile TiO₂(110) in the valence-band region measured under UHV conditions and in CO and O₂ atmosphere with a pressure of 13.3 Pa. Spectral data in panel (d, e) were acquired at beam line (BL) 13B of the Photon Factory.
barrier that carriers have to overcome on the crystal surface (Figure 4). Although this issue was thoroughly addressed by Zhang and Yates [33], very few studies have focused on surface band bending. This phenomenon can be disregarded only when the TiO\textsubscript{2} photocatalysts are in a powdered form, with a size of less than a few tens of nanometers [33]. This is because in this case, the width of the SCR is comparable to the particle size. Hence, the barrier height $V_s$, which is defined by the difference between the energy level at the surface and that in the bulk (Figure 4), is comparable to or smaller than $k_B T$, where $k_B$ and $T$ are the Boltzmann constant and temperature, respectively. However, as the particle size for bulk single crystals is larger than a few tens of nanometers, the effect of the SCR on the carrier dynamics should be taken into account.

Laser-based time-resolved measurement techniques such as transient absorption spectroscopy, photoluminescence spectroscopy, photoconductance measurements, etc., are not suitable for assessing the surface electronic structure and, thus, the band-bending structure of a TiO\textsubscript{2} photocatalyst. On the other hand, photoelectron spectroscopy is ideal for measuring the electronic structure. Thus, if this technique is used to determine the carrier dynamics, the relation between the carrier lifetime and the surface potential barrier can be discussed. Time-resolved two-photon photoelectron spectroscopy (TR-2PPE) and time-resolved X-ray photoelectron spectroscopy (TRXPS) are two current time-resolved photoelectron spectroscopy techniques. In the present contribution, we mainly focus on recent achievements in TiO\textsubscript{2} photocatalysis research using TRXPS.

III. TRXPS AND SPV

A. Time-resolved XPS

Photoelectron spectroscopy is one of the most successful experimental techniques for characterizing material properties through non-destructive, element-specific, and quantitative measurements. It can probe not only electronic structures and elemental compositions of solid surfaces [34–36] but also material conversion processes such as catalytic reactions [37]. For XPS measurements, characteristic X-rays, typically Al K\textalpha and Mg K\textalpha lines, are used as laboratory light sources, while synchrotron radiation (SR) is also available and frequently used [38]. The biggest advantage of SR over laboratory light sources is the tunable photon energy. As a result, it is possible to obtain depth-resolved measurements of the electronic structure, as demonstrated in Figure 3(d), and an elemental distribution [39]. Moreover, bulk band structures of crystals can be determined by angle-resolved photoelectron spectroscopy (ARPES) combined with photon-energy dependent measurements [40]. Resonant photoemission measurements [41, 42] and core-hole clock measurements [43, 44] are other photoelectron spectroscopy techniques where the photon energy tunability is used.

SR is an inherently pulsed radiation because it originates from individual electron bunches when they are radially accelerated by a magnet (a bending magnet) or by periodically arranged short-dipole magnets (an undulator) in a storage ring. In the A-mode operation of SPring-8, an SR facility in Japan, for example, the number of electron bunches in the storage ring is 203, with a revolution time of 4.789 $\mu$s [45, 46]. Thus, the SR pulses are provided every 23.6 ns ($= 4.789 \mu$s/203). The pulse width is determined by the electron bunch length and is typically several tens of picoseconds [45, 46].

The pulse characteristics of SR light offer a good opportunity to conduct time-resolved measurements using a pump-probe method. Here, a pump pulse generates an excited state, and its time evolution is monitored by a probe pulse (Figure 5). This method is unique in that the relaxation process of the excited state can be tracked in real time by

Figure 4: Schematic carrier diffusion in space charge regions (depletion and accumulation layers). In an upward band-bending material (a), the SCR acts as a barrier for electrons excited in the conduction band. In a downward band-bending material (b), holes in the valence band overcome the potential barrier when they reach the surface. The depletion and accumulation layers do not act as potential barriers for the holes and the electrons, respectively.

Figure 5: Schematic of the pump-probe method for time-resolved experiments.
adjusting the time difference between the pump and probe pulses, i.e., a delay time. The time resolution of the measurements is limited to the pulse width of either the pump or probe light.

The TR-2PPE technique with the pump-probe method usually uses femtosecond laser pulses in the visible and UV regions as the pump and probe lights [47]. An advantage of 2PPE is that electrons excited in the conduction bands are directly probed with a femtosecond time resolution. Hence, the dynamics of excited electrons have been successfully explored; for example, an ultrafast relaxation process in the conduction band, as demonstrated in Figure 6 [48], a single-to-triplet conversion at an organic p/n heterojunction [49], and a spin-injection process through the ferromagnet/organic semiconductor interface [50]. In TRXPS experiments, on the other hand, the femtosecond laser and the SR light in the X-ray region are combined, and photoexcited states are monitored via XPS [51, 52]. TRXPS enables us, in principle, to have a local view of the excitation state, since the core electrons are localized at the atoms that they belong to and their binding energies are sensitive to the chemical environment surrounding the atoms. This is different from 2PPE, which probes the valence and conduction states, whose wave functions are spatially extended. Thus, TRXPS is more suitable for investigating a system that has multiple components. Figure 7 demonstrates the time evolution of the excited states of C₆₀ and copper phthalocyanine (CuPc) in a CuPc/C₆₀/TiO₂(110) system, which are individually determined by analyzing the C 1s spectra [53].

The time resolution of TRXPS that uses SR light as a probe light is limited to several tens of picoseconds, even when a femtosecond laser is employed as a pump light. However, the use of an X-ray free-electron laser (XFEL) [54, 55] or high-harmonic generation (HHG) [56] as a probe light enables results in a femtosecond time resolution because they provide ultrashort pulses of a femtosecond order. A laser-pump-XFEL-probe TRXPS study successfully captured an ultrafast charge transfer (< 1 ps) from a ruthenium-based dye N₃ molecule to a ZnO substrate, by monitoring the transient chemical shift of the Ru 3d core-level peak [55].

**B. Surface photovoltage (SPV)**

The generation of a surface photovoltage (SPV) is a fundamental optical response of semiconductors when their surfaces are irradiated by light with energy higher than the band-gap energy [57]. A necessary condition for SPV generation is an SCR at the semiconductor surface. This is because the potential gradient in the SCR facilitates the dissociation of photogenerated excitons into electrons and holes, i.e., these charged particles are forced to drift in opposite directions. Separated electrons and holes in an accumulation
layer drift to the surface and the bottom of the SCR, respectively [Figure 8(a)], and vice versa in a depletion layer. Such charge separation leads to a partial or complete cancelation of the built-in electric field that induces band bending, depending on the number of separated carriers. As a result, the magnitude of band bending, namely the surface potential, is diminished by $V_{SPV}$. This is defined as the SPV and is determined experimentally from a light-induced energy-level shift on the semiconductor surface [Figure 8(b)]. It is worth noting that, except for some special cases [58], the SPV effect always results in a reduction of band bending. In other words, one can predict the type of the layers (depletion layer or accumulation layer) based on the shift direction of the energy levels.

The generation process of the SPV by an ultrashort pulse is very fast and is usually completed in less than 50 ps, irrespective of the semiconductors, because the generation process is not detected by TRXPS (which has a time resolution of ~50 ps) [59–62].

The photoexcited carriers in the flat-band region beneath the SCR contribute less to the SPV than those in the SCR. This is because electron-hole charge separation occurs only when there is thermal fluctuation; hence, a large fraction of the separated charge is lost by electron-hole recombination during thermal diffusion.

The SPV diminishes gradually with time because the carriers at the bottom of the SCR diffuse back to the surface, overcome the surface potential barrier, and recombine with the counter carriers at the surface [Figure 8(c)]. Compared with the SPV generation process, the decay process is generally slower, with time constants ranging from nanoseconds to microseconds. Figure 9 shows the SPV decay process evaluated with TRXPS measurements. When the 3.1-eV femtosecond laser pulse irradiates the graphene/SiC(0001) surface, both the C 1s and Si 2p core-level peaks move towards higher binding energies, i.e., the peaks are shifted by 0.22–0.24 eV at a delay time of 0.1 ns [62]. The shift gradually decreases, with a decay time constant of 3–4 ns, which is much slower than the generation of the SPV (< 0.1 ns).

**C. Recombination time analyzed via SPV relaxation**

Considering the decay process of the SPV in Figure 8(c), it is natural to speculate that the surface barrier height strongly influences the SPV relaxation time.

We assume that the band bending exists on the surface in dark conditions ($V_s$) (Figure 4) and that there is SPV generation with a magnitude of $V_{SPV}$ upon electron-hole separation [Figure 8(b)]. $V_{SPV}$ can be approximately expressed as [63]:

$$V_{SPV} = \frac{n_{ph}}{n_0} \exp \left( \frac{V_s}{k_B T} \right),$$

where $n_{ph}$ and $n_0$ are densities of photoexcited and intrinsic carriers (electrons or holes), respectively. $k_B$ and $T$ are the Boltzmann constant and temperature, respectively. The above equation is valid only if $V_s - V_{SPV} \gg k_B T$. Moreover, Eq. (1) tells us that $V_{SPV}$ is proportional to $\ln(n_{ph}/n_0)$ when $V_s$ and $V_{SPV}$ are much larger than $k_B T$. The value of $V_{SPV}$ is given by the following equation [63].

![Figure 8: Schematic illustration of SPV generation and decay processes in the accumulation and depletion layers. (a) Electron-hole generation upon light absorption followed by electron-hole separation. Separated carriers drift to the surface and bottom of the SCR and are trapped by a surface state. (b) SPV generation and resultant reduction of the magnitude of band bending. (c) Carrier diffusion from the bottom of the SCR to the surface, electron-hole recombination at the surface, and the resultant SPV decay.](image1.png)

![Figure 9: TRXPS profiles in (a) C 1s and (b) Si 2p core-level regions of graphene/SiC(0001). The energies of the pump laser and probe SR were 3.1 eV and 740 eV, respectively. The laser illumination induces energy shifts of both spectra as a result of SPV generation, and the SPV decays with a time constant of 3–4 ns (c, d). [Reprinted from T. Someya, H. Fukidome, N. Endo, K. Takahashi, S. Yamamoto, and I. Matsuda, Appl. Phys. Lett. 113, 051601 (2018); used in accordance with the Creative Commons Attribution (CC BY) license.](image2.png)
\[ V_{SPV} = \eta k_B T \ln \left( 1 + \gamma \frac{n_{ph}}{n_0} \right) \] (2)

Here, \( \eta \) and \( \gamma \) are constants. After generation of the SPV, the number of photoexcited carriers \( n_{ph} \) gradually decreases due to electron-hole recombination. Thus, \( V_{SPV} \) depends on the time \( t \) according to the following differential equation, derived from Eq. (2):

\[ \frac{dV_{SPV}(t)}{dt} = \eta k_B T \frac{d}{dt} \ln \left( 1 + \gamma \frac{n_{ph}}{n_0} \right) \]

\[ = \eta k_B T \frac{\gamma}{n_0 + \gamma n_{ph}} \frac{d}{dt} n_{ph} . \] (3)

\( n_{ph} \) is also a function of \( t \) and its differential equation is written as:

\[ \frac{dn_{ph}}{dt} = - \frac{n_{ph}}{\tau} . \] (4)

\( \tau \) is the carrier lifetime. The electron-hole recombination proceeds via a thermionic emission process, which is characterized by the carriers overpassing the surface potential barrier, as depicted in Figure 8(c). In this case, \( \tau \) is determined by the barrier height. The carrier lifetime in the absence of the SPV is \( \tau_\infty \) and \( \tau \) is expressed as follows [64].

\[ \tau = \tau_\infty \exp \left( - \frac{V_{SPV}}{\eta k_B T} \right) . \] (5)

\( \eta \) in Eqs. (2) and (5) is called an ideality factor [65], which is an indicator of the electron-hole recombination rate before the carriers overpass the surface potential barrier. It generally has a value between 1 and 2. By inserting Eqs. (2) and (5) into Eq. (4), we obtain the following differential equation:

\[ \frac{dn_{ph}}{dt} = - \frac{n_{ph}}{\tau_\infty} \left( 1 + \gamma \frac{n_{ph}}{n_0} \right) . \] (6)

Then, the insertion of Eqs. (2) and (6) into Eq. (3) leads to the following differential equation:

\[ \frac{dV_{SPV}(t)}{dt} = - \frac{\eta k_B T}{\tau_\infty} \left[ \exp \left( \frac{V_{SPV}}{\eta k_B T} \right) - 1 \right] . \] (7)

Eq. (7) can be analytically solved, which leads to an equation that describes the time-dependent SPV:

\[ V_{SPV}(t) = -\eta k_B T \ln \left\{ 1 - \left[ 1 - \exp \left( - \frac{V_0}{\eta k_B T} \right) \right] e^{-t/\tau_\infty} \right\} . \] (8)

Here, \( V_0 \) is the SPV at \( t = 0 \), i.e., \( V_{SPV}(0) = V_0 \). The SPV relaxation rate is described by \( \tau_\infty \), which is related to the carrier lifetime, as defined by Eq. (5). \( \tau_\infty \) is a parameter of the carrier lifetime that can be determined experimentally.

**IV. PHOTOCATALYTIC ACTIVITY**

**A. Surface science approach**

There are many factors that influence the photocatalytic activity of TiO\(_2\) (and other photocatalysts): crystal structures, crystal morphology (particle size and shape), surface orientation of the crystal, carrier doping, surrounding environments, wavelengths and powers of irradiated lights, etc. It is difficult to identify the main factor and to understand the mechanism of photocatalysis. Using practical catalysts under working conditions is essential to understand the photocatalytic activity. On the other hand, the surface science approach is more appropriate to clarify the underlying fundamental physics of photocatalysis.

The use of bulk single crystals or single crystalline films with well-defined surfaces is an example of the surface science approach. Pioneering works in this domain were conducted by the DuPont Company and Carnegie Mellon University in 1998 [66, 67]. They compared the photoelectrodegradation of Ag\(^+\) to Ag metal from an AgNO\(_3\) aqueous solution on different rutile TiO\(_2\) crystal facets under illumination of filtered mercury lamp and found that the order of photocatalytic activity was (101) > (111) ≈ (001) > (100) ≈ (110). More recently, Ahmed et al. examined the photocatalytic oxidation and hydroxylation of organic molecules on single crystal anatase and rutile TiO\(_2\) surfaces in aqueous environments and found that the anatase (101) surface exhibited higher activity than the rutile surfaces with (001), (100), and (110) orientations [18]. Luttrell et al. also reported that the anatase (001) surface had higher photodecomposition activity (of methyl orange in an aqueous solution) than the rutile (101) surface [20]. These results are in good agreement with the already recognized trend; namely, the photocatalytic activity of anatase TiO\(_2\) is superior to that of rutile TiO\(_2\) [15-17].

Another surface science approach for evaluating the crystal orientation dependence is the microanalysis of TiO\(_2\) microcrystals. Ohno et al. used a scanning electron microscope and observed a number of Pt and PbO\(_2\) deposits, which were formed by liquid-phase photocatalytic redox reactions, on each micro-size crystal in the TiO\(_2\) powder [68]. They found that the rutile (011) and anatase (001) facets hosted oxidation sites, while reduction sites were mainly on rutile (110) and anatase (011) facets. Tachikawa et al. employed a single-molecule fluorescence imaging technique to compare the photocatalytic reduction of a dye molecule on the (001) and (101) facets of a micrometer-sized anatase TiO\(_2\) crystal [69]. An interesting finding is that the (101) facet exhibited activity even when the microfocused UV light was irradiated only on the (001) facet, i.e., the (101) facet remained dark.

The work by Pan et al. somewhat combines the catalytic and surface science approaches [70]. They prepared anatase TiO\(_2\) crystal powders with predominant (001), (101), or (010) facets by controlling the synthesis parameters (concentration of reactants and reaction temperature) and compared the photocatalytic H\(_2\) evolution from a methanol solution. Although the facets terminated by fluorine atoms exhibit relatively low photoreactivity without an apparent facet dependence, a higher activity was observed on fluorine-free surfaces, with an activity order of (010) > (101) > (001) [70]. The authors have proposed that a determining factor should be a reduction potential of the excited electrons owing to a higher CBM position which depends on the crystal facets.
B. Evaluation by XPS

1. Surface preparation

Our approach to evaluate and compare the photocatalytic activity of rutile and anatase TiO$_2$ surfaces was to use bulk single crystals with well-defined low-index surfaces [71−73]. Commercially available synthetic rutile crystals with (110), (011), (100), and (001) surfaces (MTI Co.) and naturally grown anatase crystals with (001) and (101) surfaces (Surface Preparation Laboratory) were used. These surfaces were cleaned in a UHV chamber via cycles of Ar$^+$ sputtering (1−2 kV, $1 \times 10^{-4}$ Pa Ar, 10 min) and annealing in an O$_2$ atmosphere [(1−2.5) $\times 10^{-4}$ Pa O$_2$, 900 K, 10 min] until no carbon contamination was detected by XPS or Auger electron spectroscopy (AES) measurements.

The clean TiO$_2$ surfaces had low-energy electron diffraction (LEED) patterns, as shown in Figure 10. The (1×1) patterns were observed on the (110), (100), and (001) surfaces of rutile TiO$_2$ as well as on the anatase TiO$_2$(101) surface. The other two surfaces are known to undergo characteristic reconstructions; the rutile TiO$_2$(011) surface [also referred to as the (101) surface in literature] develops a (2×1) reconstructed structure, whose atomic arrangement has been extensively debated [74, 75], whereas a well-known 4×1/1×4 double domain structure is developed on anatase TiO$_2$(001) [76]. The LEED patterns on these surfaces shown in Figure 10 support these surface reconstruction concepts.

2. Acetic acid adsorption

The photocatalytic activity of single-crystal TiO$_2$ surfaces was assessed by UV-induced decomposition of adsorbed molecules. We chose acetic acid as a probe molecule, whose decomposition by the UV light was qualitatively monitored by XPS. The XPS measurements was carried out at beam line (BL) 13B of The Photon Factory [77] using a SES200 photoelectron energy analyzer (Gamma Data/Sciencta) (Figure 11).

The adsorption of acetic acid was conducted in a loadlock chamber with a base pressure lower than $1 \times 10^{-6}$ Pa. The TiO$_2$ samples were placed in the presence of acetic acid vapor. The samples were kept at room temperature during adsorption process. The exposure amounts were between 10 L and 20 L (Langmuir; 1 L = $1.3 \times 10^{-4}$ Pa s), which are sufficient for adsorption saturation [78−80].

Acetic acid is known to adsorb on TiO$_2$ surfaces in the form of acetate (CH$_3$COO$^-$). On rutile TiO$_2$(110), the two O atoms of acetate are bonded to the five-coordinated surface Ti atoms (Ti$_{5c}$) [Figure 12(a)] with a saturation coverage of 0.5 ML (monolayer; 1 ML is defined as the density of the five-coordinated Ti atoms, i.e., $5.2 \times 10^{14}$ cm$^{-2}$) [79]. Figure 12(b) shows the XPS profiles in the C 1s and valence band regions of the acetate-adsorbed rutile TiO$_2$(110) surface. The C 1s spectra show two peaks, at 285.8 eV and 289.2 eV, which are associated with methyl carbon and carboxylate...
carbon, respectively. The adsorption process induces a shift of the TiO$_2$ valence band toward higher binding energies [lower panel in Figure 12 (b)], which results in a more intense band-gap state just below the Fermi level. This suggests an increase in the density of reduced Ti, i.e., Ti$^{3+}$, in the surface region, since the band-gap state originates from the Ti 3d state of Ti$^{3+}$ species, which are inevitably formed by the loss of bridging O atoms [81] when the clean surface is prepared under UHV conditions. O$_2$ adsorption effectively compensates the defects in the bridging O rows so that the band-gap state is suppressed, as shown in Figure 3(e). However, O defects are not compensated by acetate. On the contrary, our observation implies a partial charge transfer from acetate to the surface Ti atoms through acetate−Ti$^{5+}$ bonds. This result is in contrast with an earlier report on the same system [79], where acetic acid adsorption suppresses the band-gap state. A possible explanation is that acetate can occupy the O defects when the defect density is high; this is based on the fact that the band-gap state intensity is higher on the surface studied in Ref. 79 than on our prepared surface. We also observed this adsorption-induced suppression of the band-gap state in another study [73], which examined the adsorption on a rutile TiO$_2$(110) defective surface.

The amount of adsorbed acetic acid depends on the surface orientation of the TiO$_2$ crystals (Figure 13). Among the rutile surfaces, the (100) surface can accommodate the largest amount of acetic acid (0.63 ML), followed by the (110) surface (0.50 ML), the (001) surface (0.45 ML), and the (011) surface (0.41 ML). The saturation coverages are similar on the two anatase TiO$_2$ surfaces, with 0.56 ML and 0.54 ML on the (101) and (001) surfaces, respectively. The order of the saturation coverage reflects the order of chemical reactivity toward acetic acid adsorption. Thus, the rutile TiO$_2$(100) surface has the highest chemical activity among the six TiO$_2$ surfaces.

We also examined the adsorption activity of a defective surface. The defective surface was prepared by Ar$^+$ sputtering (1.25 kV in 6 × 10$^{-6}$ Pa for 10 min) of a clean rutile TiO$_2$(110) surface. The defect density, estimated from the analysis of the Ti 2p XPS profile, was 2 × 10$^{14}$ cm$^{-2}$ [73]. This corresponds to 38% of the density of the bridging O atoms. The defective surface exhibits an even higher adsorption activity, with a saturation coverage of 0.66 ML, compared to rutile TiO$_2$(100). The high density of the defects apparently facilitates acetic acid adsorption.

3. Effect of UV irradiation

The photocatalytic activity of the TiO$_2$ catalysts is usually evaluated by the reaction rates of molecules and ions in gas phases [6, 69] or in solutions [1–5, 7, 15–18, 20, 66–68, 70]. On the other hand, direct measurements of molecules adsorbed on the catalyst surfaces have also been used to assess the photocatalytic activity [19, 78]. In our study, the photocatalytic activity of rutile and anatase TiO$_2$ surfaces under UHV was evaluated through the UV-induced decrease of the amount of adsorbed acetic acid, i.e., by monitoring the C 1s XPS peak intensity [73].

A continuous-wave UV laser with a wavelength of 375
nm (3.31 eV) was used to irradiate acetate-saturated TiO₂ surfaces. The laser was delivered with a power of 2.4 W cm⁻² by a diode module (Obis 357LX, Coherent Inc.). The module was mounted on an x-y stage, which was attached to a MgF₂ viewport on the back side of the SES200 analyzer (Figure 11). The UV laser, thus, irradiated the sample surface through an analyzer slit and analyzer lens. The C 1s XPS profiles of the sample surfaces were obtained using SR with an energy of 753 eV as an excitation source. The spot size of the laser had a diameter of 1.6 mm on the sample surface [73], while the irradiation area of the SR light, whose incidence angle was 65° from the sample normal direction, was 310 μm × 40 μm [77]. The spatial overlap between the laser and the SR light was confirmed by the large Si 2p XPS peak shift of a Si(111) wafer (70 meV toward a higher binding energies) as a result of UV-induced SPV [73].

UV-laser irradiation leads to a gradual intensity decrease of the acetate C 1s peaks. Figure 14 shows two examples. The spectra in Figure 14(a, d) show the time-dependent changes of the C 1s peaks of acetic acid-saturated rutile TiO₂(001) and anatase TiO₂(101) surfaces under irradiation by the UV laser. The peak intensities are diminished to ~80% of their original intensities after approximately 1 h of irradiation on both surfaces. However, the UV-induced photocatalytic decomposition/desorption of acetate is not the only cause of the peak intensity decrease. As shown in Figure 14(b, e), the intensity decrease is also observed even when the UV laser is not active. Thus, the SR light causes damage to acetate molecules on TiO₂; this should be distinguished from photocatalytic decomposition.

The decrease in the peak intensity induced by simultaneous irradiation of UV laser and SR light is apparently higher than that induced by irradiation of SR light alone [Figure 14(c, f)]. The same behavior was also observed on other...
To quantitatively evaluate the contribution of photocatalysis, we study the difference between the UV-on and UV-off data of the C 1s peak intensities [Figure 14(c, f)]. In Figure 15, the net changes of the C 1s intensity on six TiO₂ surfaces are shown. The C 1s peak intensity is diminished on four surfaces, while no change is observed on rutile TiO₂(100) and (011) surfaces. The two latter surfaces are inactive with regard to the photocatalytic decomposition of acetate. A more interesting finding is that, among the four photocatalytically active surfaces, the activity depends on the surface orientation. The solid lines in Figure 15 are the best-fitted functions of the photocatalytic decomposition/desorption of acetate. The fitting is accomplished by the exponential function, where the photocatalytic activity is not the most important factor that influences the photocatalytic activity of TiO₂.

A fundamental question is why the photocatalytic activity differs depending on the crystal surfaces rather than the bulk crystal structures. Moreover, it is apparent that the order of the photocatalytic activity (Table 2) is not correlated with the surface chemical activity (Figure 13). To answer this question, we evaluated the photoexcited carrier lifetime on each TiO₂ surface and verified the relation between the carrier lifetime and photocatalytic activity.

V. CARRIER LIFETIME

A. Lifetime determined by TRXPS

As mentioned in Section III.C, the lifetimes of photoexcited carriers are determinable from transient changes of the SPV. The SPV on the TiO₂ surfaces after UV-laser pulse irradiation was evaluated by a transient shift of the Ti 2p spectrum [71, 72]. We examined the carrier lifetime for each TiO₂ surface; anatase TiO₂(001), rutile TiO₂(110), rutile TiO₂(011), and defective rutile TiO₂(110). An example of TRXPS measurement results is shown in Figure 16(a). Here, the change in the Ti 2p spectrum of anatase TiO₂(001) as a function of delay time is demonstrated.

The TRXPS measurements utilizing the pump-probe method were carried out at BL07LSU of SPring-8 [82]. A second harmonic of an amplified Ti:sapphire laser (405 nm = 3.06 eV) was used as a pump light. The pulse duration of the laser was 35 fs and the repetition rate was 1 kHz. The power densities of the pump laser were typically between 12 and 48 mJ cm⁻² pulse⁻¹. For the probe light, a 600-eV SR light was used. The operation modes of the storage ring were an F mode (a 1/14-filling bunch train and 12 bunches) and an H mode (11/29-filling bunch train and a single bunch), and SR pulses from isolated bunches were used for the probe light. The SR pulse duration was approximately 50 ps, which is the time resolution of the TRXPS measurements. Photoelectron energies were analyzed by a time-of-flight electron spectrometer (VG Scienta ARTOF 10k).

The Ti 2p₃/₂ peak of anatase TiO₂(001) moves toward TiO₂(001), and anatase TiO₂(001). This order should reflect the photocatalytic activity. Rutile TiO₂(110) and (011) are photocatalytically inactive, with \( \tau_{\text{ph}} = 0 \text{ min}^{-1} \).

We also verified the photocatalytic activity on a defective surface. The defective surface was prepared by lightly sputtering a rutile TiO₂(110) surface that had surface O vacancies (with a density of roughly 2 × 10¹⁴ cm⁻²) [73]. Since such vacancy sites are generally active during molecular adsorption, a higher saturation coverage is achieved on the defective surface than on the pristine surface, as shown in Figure 13. However, the defective rutile TiO₂(110) surface has a lower photocatalytic activity than the pristine surface. \( \tau_{\text{ph}} \) is determined to be 2100 min and, thus, \( k_{\text{ph}} = 5 \times 10^{-3} \text{ min}^{-1} \), which is less than 1/5 of the value for pristine rutile TiO₂(110). This result implies that the surface chemical activity is not the most important factor that influences the photocatalytic activity of TiO₂.

Table 2: Decay time constant of the C 1s peak intensity (\( \tau_{\text{ph}} \)) and rate constant of the photocatalytic decomposition/desorption of acetate (\( k_{\text{ph}} \)).

| Polymorph       | Surfaces | \( \tau_{\text{ph}} \) (min) | \( k_{\text{ph}} \) (min⁻¹) |
|-----------------|----------|-------------------------------|-----------------------------|
| Rutile TiO₂     | (001)    | 580                           | 1.7 × 10⁻³                   |
|                 | (110)    | 370                           | 2.7 × 10⁻³                   |
|                 | (100)    | ∞                             | 0                           |
|                 | (011)    | ∞                             | 0                           |
| Rutile TiO₂     | (110)⁺   | 2100                          | 0.5 × 10⁻³                   |

| Anatase TiO₂    | (101)    | 480                           | 2.1 × 10⁻³                   |
|                 | (001)    | 600                           | 0.5 × 10⁻³                   |

⁺Ar⁺-sputtered surface.
lower binding energies, by 0.2 eV for a delay time of 0.2 ns; the magnitude of this shift diminishes with time [Figure 16(a)]. The transient peak shift is attributed to the SPV. The direction of the shift (toward lower binding energies) indicates that an accumulation layer is formed on the anatase TiO\textsubscript{2}(001) surface. This UV-induced peak shift toward lower binding energies is also observed on rutile TiO\textsubscript{2}(110) and (011) surfaces. Thus, accumulation-type SCRs are formed on these TiO\textsubscript{2} surfaces. This is reasonable because electron-donating O vacancies are unavoidable on TiO\textsubscript{2} surfaces that are subjected to surface cleaning in UHV conditions.

Figure 16(b) shows the delay times of the SPV shifts on anatase TiO\textsubscript{2}(001) and rutile TiO\textsubscript{2}(110) and (011). The delay time on the Ar+-sputtered rutile TiO\textsubscript{2}(110) surface is also shown. On all four surfaces, the SPV decreases as the delay time is prolonged, reflecting the decrease in the number of photoexcited electrons and holes with time due to electron-hole recombination (Figure 8). However, the decreasing rate differs depending on the surface; the SPV on rutile TiO\textsubscript{2}(011) is swiftly diminished to zero within several ns, whereas much slower decreases are observed on other surfaces. These SPV behaviors should reflect the electron-hole recombination rate and, thus, the carrier lifetime. Namely, photoexcited carriers have a short lifetime on rutile TiO\textsubscript{2}(011), while the carriers survive for much longer on the other three surfaces.

For a quantitative evaluation of the carrier lifetime, the delay-time dependent SPV curves were fitted by Eq. (8). In the fitting procedure, the ideality factor $\eta$ was fixed at 1.4 [72] and $V_0$ (the SPV at $t = 0$ ns) and $\tau_\infty$ (the relaxation time in the absence of the SPV) were treated as variables. The sample temperature was $T = 300$ K. The best-fitted curves obtained from least-square fitting are shown as thick solid lines in Figure 16(b). The obtained $\tau_\infty$ values are 90 ns, 1.3 ns, 150 ns, and 230 ns for anatase TiO\textsubscript{2}(001), rutile TiO\textsubscript{2}(011), rutile TiO\textsubscript{2}(110), and defective rutile TiO\textsubscript{2}(110), respectively. These values are shown in Table 3.

As discussed in Ref. 72, several factors influence the carrier lifetime, i.e., $\tau_\infty$. These are surface potential barrier height $V_s$ (Figure 4), carrier-capture cross-section, thermal velocities of the carriers, and densities of the carrier trap states. Among these factors, the surface potential barrier height has the most significant influence on the carrier lifetime. In the next section, we discuss the relation between the lifetime and the barrier height.

### B. Lifetime on modified surfaces

The carrier lifetime $\tau_\infty$ depends on the surface potential barrier height $V_s$, as follows [72]:

$$\tau_\infty = \frac{W_{SCR}}{S_p} \exp\left(\frac{V_s}{\eta k_B T}\right).$$

Here, $W_{SCR}$ and $S_p$ are the width of the SCR and the surface recombination velocity, respectively. Since $\tau_\infty$ depends on $V_s$, exponentially, a small change in $V_s$ leads to a large change in $\tau_\infty$, whereas changes in $W_{SCR}$ and $S_p$ have a lower effect on $\tau_\infty$. Thus, if the surface condition is modified and the magnitude of surface band bending is altered, i.e., the $V_s$ value is changed, $\tau_\infty$ differs from those listed in Table 3.
This fact complicates the situation when the photocatalytic activity is discussed on the basis of the photoexcited carrier behavior.

In our study, we verified the photocatalytic activity of TiO₂ on acetate-covered surfaces, whereas the carrier lifetime was measured on adsorbate-free surfaces. Thus, we should estimate the carrier lifetimes on acetate-covered surfaces. This can be done if the adsorption-induced band bending is experimentally determined. Figure 17 compares the valence-band spectra of clean (dashed lines) and acetate-covered (solid lines) TiO₂ surfaces. Acetic acid adsorption modifies the spectral line shape and seems to push the TiO₂ band down to the higher binding energy side, as judged from the position of the VBM. The accumulation layers are already formed on the clean TiO₂ surfaces, as mentioned in Section V.A. Thus, the adsorption enhances downward band bending and, hence, the surface potential barrier height. The adsorption-induced changes of the barrier height ΔVₘ are 0.05 eV, 0.06 eV, and 0.04 eV for anatase TiO₂(001), rutile TiO₂(011), and rutile TiO₂(110), respectively. On the sputtered surface, on the other hand, the VBM position is hardly affected by adsorption.

Now, we can estimate the carrier lifetime on the acetate-saturated surface (τᵥᵥ,Ac) using the following equation [73]:

\[ \tauᵥᵥ,Ac = \tauᵥᵥ,∞ \exp \left( \frac{\Delta Vₘ}{\eta k_B T} \right). \]  

(11)

This equation is obtained from Eq. (10) under the assumption that changes in η, W_SCL, and Sₚ are negligibly small before and after acetic acid adsorption. The calculated τᵥᵥ,Ac are 360 ns, 7 ns, and 450 ns on acetic-acid saturated surfaces of anatase TiO₂(001), rutile TiO₂(011), and rutile TiO₂(110), respectively.

Regarding the defective rutile TiO₂(110) surface, the situation is not straightforward, because the O defect densities were not the same for the surface used for photocatalytic activity measurements (2 × 10¹⁴ cm⁻²) and that used for carrier lifetime measurements (3 × 10¹⁴ cm⁻²) [73]. The larger density results in a deeper VBM position because of a larger magnitude of band bending. The VBM was 3.55 eV on the surface used for carrier lifetime measurements, whereas it was 3.50 eV on the surface used for photocatalytic activity measurements [73]. If the VBM is unaffected when the defective surfaces are covered with acetate, as shown in Figure 17, the ΔVₘ value should be −0.05 eV. Therefore, the carrier lifetime on the acetate-covered defective surface is calculated to be τᵥᵥ,Ac = 60 ns. The ΔVₘ and τᵥᵥ,Ac values are also listed in Table 3.

### VI. ACTIVITY-LIFETIME CORRELATION

Photocatalytic reactions are generally complex and many elemental steps contribute to the overall reaction path. However, all photocatalytic reactions are initiated by the chemical species adsorbed on the TiO₂ surface capturing photoexcited electrons and holes. If this initial step is a rate-determining step, the reaction rate of the photocatalysis can be approximated as:

\[ \frac{d[A]}{dt} = k[c][A]. \]  

(12)

[A] and [c] are the adsorbate coverage and carrier concentration on the surface, respectively, and k is a rate constant. In the case of acetate decomposition/desorption, the hole capture by acetate is the initial step (Section IV.B.3). Thus, [A] is the acetate coverage and [c] is the hole concentration on the surface. Both [A] and [c] can be determining factors for the photocatalytic activity.

In our study, we evaluated the surface reactivity of acetic acid adsorption (acetate coverage [A]), carrier lifetime (τᵥᵥ,Ac), and photocatalytic activity (kᵥᵥ) on four TiO₂ surfaces. Figure 18 shows the relationship among these param-

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**Table 3: Carrier lifetime on adsorbate-free surfaces (τᵥᵥ), acetic-acid adsorption-induced change in surface potential barrier height (ΔVₘ), and expected carrier lifetime on the acetate-saturated surfaces (τᵥᵥ,Ac).**

| Surfaces          | τᵥᵥ (ns) | ΔVₘ (eV) | τᵥᵥ,Ac (ns) |
|-------------------|---------|---------|------------|
| anatase TiO₂(001)| 90      | 0.05    | 360        |
| rutile TiO₂(011) | 1.3     | 0.06    | 7          |
| rutile TiO₂(110) | 150     | 0.04    | 450        |
| rutile TiO₂(110) | 230     | −0.05   | 60         |

*Ar⁺-sputtered surface.

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**Figure 17:** Valence-band spectra of TiO₂ surfaces. Dashed and solid lines indicate the spectra of the clean and acetate-saturated surfaces, respectively. The spectra were acquired at BL-13B of the Photon Factory. The photon energy was 100 eV.
eters. It is apparent that there is a linear and positive correlation between $k_{ph}$ and $\tau_{\infty,Ac}$, whereas no correlation is observed between $k_{ph}$ and $[A]$. Since a longer lifetime leads to higher carrier concentration on the surface, it is natural to correlate $\tau_{\infty,Ac}$ with $[c]$. Therefore, regarding the photocatalytic decomposition/desorption of acetate, the carrier lifetime and resultant accumulation of carriers on the surface are major factors that influence the photocatalytic activity.

It should be noted that intensities of the UV lasers used in our study are much higher than the UV light intensity in the sunlight. For example, a time-averaged photon flux of the 405-nm pulsed laser with a power density of 12 mJ cm$^{-2}$ pulse$^{-1}$, which was used to determine the SPVs on anatase TiO$_2$(001) and rutile TiO$_2$(110) (Figure 16), is in the order of $10^{17}$ photons mm$^{-2}$ s$^{-1}$, which is larger by four to five orders of magnitude than the photon flux of the 400-nm light in the sunlight. Namely, TiO$_2$ photocatalysts under the sunlight work in a very weak excitation condition. It is known that the dynamics of the photoexcited carriers differs depending on the carrier concentration, i.e., the excitation condition [84]. Nevertheless, the essence of the carrier dynamics is kept intact as depicted in Figure 2. Thus, the correlation between the carrier lifetime and the photocatalytic activity could be also be found under the weak excitation condition.

Another important implication noticed from Figure 18 is that anatase TiO$_2$ is not always more active than rutile TiO$_2$. The surface potential barrier height $V_s$ is the most influential parameter for the carrier lifetime, as inferred from Eq. (10). Thus, a TiO$_2$ surface having a large $V_s$ in the working condition should have a chance to exhibit a high photocatalytic activity regardless of the bulk structure. In other words, the photocatalytic activity is controllable through surface modification and the resulting change in $V_s$.

It is worth mentioning that the importance of $V_s$ is lessened when the size of the photocatalysts is reduced to the nanometer. Zhang and Yates pointed out in their review paper [33] that band bending is negligible in nanoparticles with a diameter of less than 10 nm. In this case, the carrier trap process by defect states is more important for the carrier lifetime. Morgan and Watson theoretically verified the defect formation in anatase and rutile TiO$_2$ crystals and found that the O defect formation is more favorable in anatase TiO$_2$ than in rutile TiO$_2$ [85]. Thus, we can speculate that anatase has a longer carrier lifetime than rutile in the form of nanocrystals.

One of our conclusions deduced from preceding previous study [71] is that the carrier lifetime is expected to be longer on anatase TiO$_2$(001) than on rutile TiO$_2$(110) in the absence of a surface potential barrier. This trend can be explained by the different type of bulk band gap (direct and indirect band gaps); however, the different defect concentration in the bulk of the crystals should also be taken into account. A more detailed discussion on the determining factors of carrier lifetime beyond the surface barrier potential can be found in Ref. 72.

VII. CONCLUDING REMARKS

An increasing demand for clean and renewable energy, in order to develop a sustainable society, has accelerated the research and development of photocatalysts. TiO$_2$ has been the most extensively studied photocatalyst for nearly half a century [1, 2, 9–12], and considerable progress has been achieved in understanding various photocatalytic phenomena. One of the most interesting properties of TiO$_2$ photocatalysis is the crystal-structure dependence of the photocatalytic activity, namely, a higher activity of the anatase form compared to that of the rutile form [15–20]. Another striking feature is the fact that crystal surfaces with different orientations exhibit different photocatalytic activities [18, 20, 66–70]. Both catalytic and surface-science techniques have been employed to establish a precise view of these photocatalytic properties.

The surface-orientation dependence is purely a surface phenomenon, since the bulk structure is identical. An often employed explanation is that each surface has a different chemical reactivity and hence, the photocatalytic activity depends on the surface orientation. On the other hand, pho-

![Figure 18](image.png)

*Figure 18: Photocatalytic activity $k_{ph}$ as a function of (a) acetate coverage $[A]$ and (b) carrier lifetime $\tau_{\infty,Ac}$. The solid line in panel (b) is the result of least-square fitting.*
to excited carriers also contribute to the surface-dependent activity. The carrier behavior is complex, especially in the near-surface region where a charge accumulation layer or a depletion layer is developed, because these space charge layers act as a surface potential barrier for electrons or holes when they diffuse from the bulk to the crystal surface [33]. Thus, if the relationship among the chemical reactivity, the carrier behavior, and the photocatalytic activity is clarified on each crystal surface, it will provide a significant insight on the mechanism of the surface-dependent photocatalytic activity and, thus, on the general photocatalysis mechanism of TiO$_2$.

We employed a surface science approach to study this problem [71–73]. Using well-defined surfaces of anatase and rutile TiO$_2$ single crystals, the chemical activity of acetic acid adsorption, lifetime of photoexcited carriers, and photocatalytic decomposition/desorption of adsorbed acetic acid were examined by XPS and TRXPS under UHV conditions. The chemical activity was assessed by the saturation amount of adsorbed acetic acid. The carrier lifetime was determined by temporal evolution of the UV-induced SPV. The photocatalytic activity was estimated via the time-dependent intensity decrease of the acetate C 1s XPS peak, a result of the UV-induced decomposition/desorption of acetate. Although there is no correlation between the photocatalytic activity and chemical reactivity, the photocatalytic activity is linearly and positively correlated with the carrier lifetime. This result indicates that the carrier lifetime is a more influential factor than the chemical activity of the photocatalyst surface with regard to the photocatalytic activity of acetic acid.

Another interesting finding is that the crystal structure of TiO$_2$, i.e., anatase or rutile polymorph, is not a decisive factor [72] despite the prediction that the bulk carrier lifetime is longer in the anatase crystal than in the rutile crystal (owing to the bulk band structure [19] and/or the difference in the defect concentration in the bulk [85]). Instead, the potential carrier behavior is complex, especially in the near-surface region where a charge accumulation layer or a depletion layer is developed, because these space charge layers act as a surface potential barrier for electrons or holes when they diffuse from the bulk to the crystal surface [33]. Thus, if the relationship among the chemical reactivity, the carrier behavior, and the photocatalytic activity is clarified on each crystal surface, it will provide a significant insight on the mechanism of the surface-dependent photocatalytic activity and, thus, on the general photocatalysis mechanism of TiO$_2$.

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