How important is the surface potential barrier to determine the lifetime of photoexcited carriers on TiO_2 photocatalysts?: Time-resolved photoelectron spectroscopy study

Since Fujishima and Honda discovered the electrochemical photolysis of water at the titanium dioxide (TiO_2) electrode in 1969 [1], extensive efforts have been devoted to elucidate physics behind the superior photocatalytic properties of TiO_2. Photocatalytic reactions are initiated by the interaction of photoexcited carriers (electrons and holes) with chemical species on the catalyst surface (Fig. 1). Thus, the efficiency of photocatalysis should depend on the carrier lifetime, which is determined by a balance between electron-hole separation and electron-hole recombination processes.

TiO_2 crystals with anatase and rutile structures are usually used as photocatalysts. The different carrier lifetimes of the polymorphs suggest that anatase is more photocatalytically active than rutile [2]. However, the experimentally determined lifetimes range from picoseconds to microseconds. Although the measurement conditions, such as temperatures, surrounding environment, crystal size, etc., are known to affect the lifetime, there is no reasonable explanation for the diversity of the reported values. What governs the carrier lifetime is an important question that must be answered in order to comprehensively understand the photocatalytic activity of TiO_2.

A major difficulty in carrier dynamics studies is assessing the effect of the space charge layer (SCL) on the carrier behavior. In the SCL, the band positions vary energetically when going from the bulk to the surface, and this energy difference is viewed as a potential barrier for charged particles. Photoexcited carriers must overcome the surface potential barrier as they are transported to the surface to initiate chemical reactions (Fig. 1). Thus, the surface potential should significantly influence the photocatalytic activity via the carrier lifetime. However, most studies do not take the role of the SCL into account when discussing the activity from the carrier dynamics point of view [2].

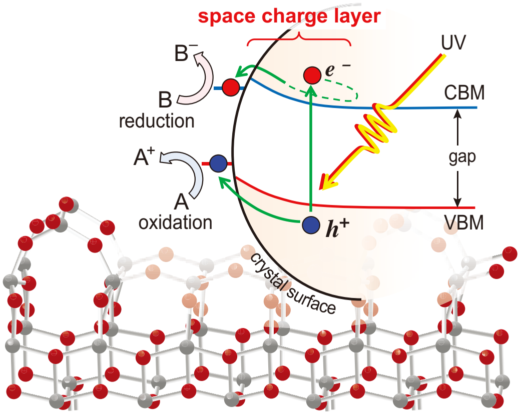
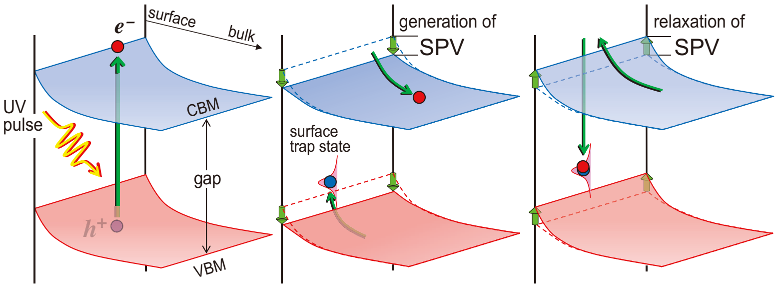


Fig. 1. Schematic of the carrier dynamics on a photocatalyst surface from photoexcitation to redox reactions.

To clarify the role of the surface potential in the SCL, time-resolved (TR) photoelectron spectroscopy (PES) was utilized to measure the carrier lifetime on single-crystalline anatase and rutile surfaces [3]. Compared to other transient measurement techniques, e.g., photoluminescence spectroscopy, absorption spectroscopy, and photoconductivity measurements, this technique is advantageous because the carrier lifetime and potential barrier height can be determined, allowing correlations between these two factors to be estimated. The TR-PES measurements were carried out at **BL07LSU** utilizing the laser-pump/synchrotron-radiation-(SR)-probe method [4]. A second harmonic of an amplified Ti:sapphire laser (the photon energy of 3.06 eV with a pulse width 35 fs) was used to generate excited carriers, and 600-eV SR pulses were employed to measure the PES spectra. The laser pulse excites the valence electrons to the conduction band, generating the electron-hole pairs (Fig. 2(a)). The electrons and holes are spatially separated by the electric field within the SCL; one drifts to the surface and is trapped by the surface-trap states, and the other is transported to the bulk (Fig. 2(b)). The charge separation induces a surface photovoltage (SPV), whose magnitude diminishes over time as the density of the surface-trapped carriers decreases due to the recombination process. The counterpart carriers are thermally diffused to the surface by overpassing the potential barrier (Fig. 2(c)). We examined the time-dependent change of the SPV by measuring the temporal variations of the energy shift in the PES spectra.

Figure 3(a) shows the energy shifts of the Ti $2p_{3/2}$ core-level peaks of the anatase $TiO_2(001)$ and rutile $TiO_2(110)$ surfaces. Large shifts of 0.1–0.2 eV are induced after a 0.2 ns delay time due to the time interval between the pump and probe pulses but the magnitude of the shifts decreases gradually over the time range of about 100 ns. The estimated relaxation times (τ_s) of the SPV are 50 ± 30 ns for anatase and 180 ± 100 ns for rutile. Here, τ_s is defined as the relaxation time of the SPV in the dark condition; namely, it is the hypothetical lifetime of the trapped carriers on the crystal surface with a potential barrier height (V_s) in the absence of the SPV [3]. On the anatase and rutile surfaces, the charge



(a) ***e-h*** **pair creation** **(b)** **charge separation** **(c)** ***e-h*** **recombination**

Fig. 2. Energy band diagram of the surface photovoltage (SPV) effect. **(a)** Photoexcitation of the electron-hole (*e-h*) pair; **(b)** charge separation and the generation of the SPV, and **(c)** SPV relaxation by charge recombination.

accumulation layers are formed with V_s values of 0.2 and 0.4 eV, respectively. The larger τ_s for rutile is surely a consequence of the larger V_s due to the smaller probability of the counterpart carriers overcoming the potential barrier. If we compare the carrier lifetimes on both surfaces with the same V_s, the carrier lifetime on the anatase surface is always larger than that on the rutile surface (Fig. 3(b)). The surface-trapped carriers with longer lifetimes are more likely to encounter adsorbed species and initiate chemical reactions. This is in accordance with the well-known tendency that anatase TiO_2 is photocatalytically more active than rutile TiO_2.

Another important implication in Fig. 3(b) is that the carrier lifetime varies from picoseconds to microseconds depending on V_s. Thus, strategy to enhance the photocatalytic activity is to enlarge V_s, for example, by chemically modifying the crystal surface. Such a potential-barrier engineering is also applicable for photovoltaics, where the charge separation efficiency and the carrier lifetime are determining factors for photoelectric conversion efficiency.

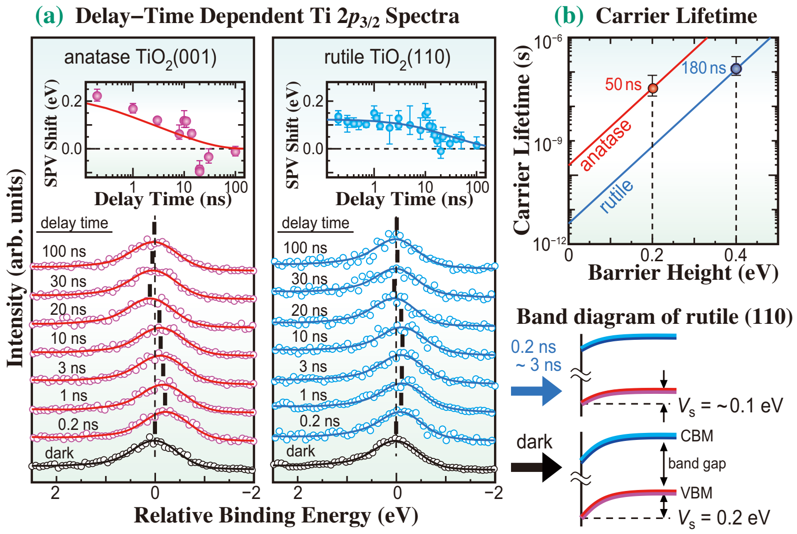


Fig. 3. **(a)** Change in the Ti $2p_{3/2}$ spectra of anatase $TiO_2(001)$ and rutile $TiO_2(110)$ as a function of the delay time. Pump and probe lights are a 3.06-eV laser with a power density of 12 mJ/cm^2/pulse and a 600-eV SR light, respectively. Insets show the relaxation of the SPV shift. Energy band diagrams of the rutile surface in a dark condition. Lower right shows those at the delay times between 0.2 and 3 ns. **(b)** Potential-barrier-height dependence of the carrier lifetimes on the anatase (001) and rutile (110) surfaces.

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