

Photocatalytic Activity of Anatase and Rutile TiO₂ Surfaces and Its Correlation with Lifetime of Photoexcited Carriers

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1 Introduction

One of many interesting aspects that TiO₂ photocatalysts exhibit is a morphology dependence of the photocatalytic activity; anatase TiO₂ (a-TiO₂) generally shows a higher activity than rutile TiO₂ (r-TiO₂). On the other hand, it has also been known that the TiO₂ photocatalytic activity depends on the orientation of the crystal surfaces. Although several mechanisms such as a surface-dependent redox potential, anisotropic diffusion of the carriers, etc. have been proposed as a possible origin of the orientation dependence, none of them explains comprehensively the phenomenon. In the present study, we systematically assessed the photocatalytic activity and photoexcited carrier lifetime on single-crystal a-TiO₂(101) and (001) surfaces and r-TiO₂(110), (001), (011), and (100) surfaces by X-ray photoelectron spectroscopy (XPS) and time-resolved XPS (TRXPS) and verified the activity-lifetime relation [1].

2 Experimental

The photocatalytic activity was evaluated by a rate constant of a photocatalytic decomposition of acetic acid. Acetic acid adsorbs in the form of acetate, and the rate of the photocatalytic decomposition of acetate was estimated from a decreasing rate of the C 1s XPS peak intensity while the ultraviolet (UV) laser with an energy of 3.31 eV was irradiated. The carrier lifetime was determined from a time evaluation of the UV-induced surface photovoltage (SPV). The SPV resulted in the shift of the valence and core levels of TiO₂. We examined the SPV via a shift of the Ti 2p level. The measurements were done at BL-13B of PF (XPS) and BL07LSU of SPring-8 (TRXPS).

3 Results and Discussion

The intensity of the C 1s peak of adsorbed acetate decreases exponentially upon irradiation of the UV light with a time constant τ_{ph} of 370 min on r-TiO₂(110) (Fig. 1). Since the reciprocal of τ_{ph} is a rate constant k_{ph} , k_{ph} on r-TiO₂(110) is evaluated to be $2.7 \times 10^{-3} \text{ min}^{-1}$. This is the largest rate constant among all surfaces examined in the present study. k_{ph} on a-TiO₂(101) and (001) are $2.1 \times 10^{-3} \text{ min}^{-1}$ and $1.7 \times 10^{-3} \text{ min}^{-1}$, respectively, while r-TiO₂(011) and (001) are inactive with $k_{ph} = 0 \text{ min}^{-1}$.

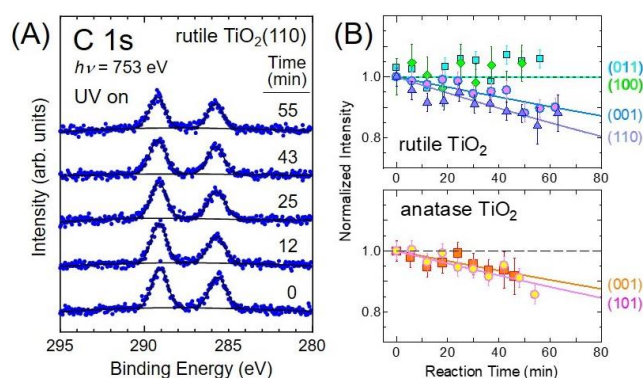


Fig. 1 (A) C 1s spectra of adsorbed acetic acid on r-TiO₂(110) at various UV-irradiation times. (B) Plot of the C 1s intensity against the UV-irradiation time.

Regarding the carrier lifetime, we examined four TiO₂ surfaces [r-TiO₂(110), r-TiO₂(011), a-TiO₂(001), and sputtered r-TiO₂(110)] without adsorbed acetate [2]. The determined lifetimes were converted to barrier-height-corrected lifetimes so as to reproduce the lifetimes on the acetate-saturated surfaces; they are 450 ns, 360 ns, and 7 ns for r-TiO₂(110), a-TiO₂(001), and r-TiO₂(011), respectively.

The lifetime is found to be proportional to k_{ph} . A plot of k_{ph} against the lifetime gives a linear and positive straight line (Fig. 2). This correlation indicates that the carrier lifetime should be a key factor to understand various properties of TiO₂ photocatalysis, including the orientation-dependent activity.

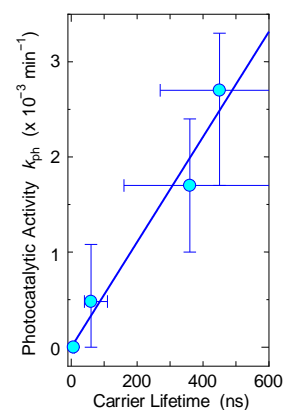


Fig. 2 Correlation between the carrier lifetime and the photocatalytic activity.

[1] K. Ozawa *et al.*, *J. Phys. Chem. C* **122**, 9562 (2018).

[2] K. Ozawa *et al.*, *J. Phys. Chem. C* **120**, 29283 (2016).

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