

# $\mu$ SR investigation of atomic structure and photocatalytic properties of defects in rutile $\text{TiO}_2$ crystal

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Photocatalysis is a promising process to solve the environmental pollution problem and energy crisis, resulting in a sustainable society.  $\text{TiO}_2$  is the most widely used material for high efficiency photocatalysis. Since the discovery of the Honda-Fujishima effect,<sup>1)</sup> many researches have been carried out to understand the key factor for the photocatalytic activities. Since photocatalysis systems are complex, their nature is strongly affected by the crystal structure, surface area, number of surface hydroxyls, defect sites, and so on. Defect sites are one of the most significant factors that determine the photocatalytic activities. However, the characterization of defect sites has not been established yet, since in most cases several types of defect sites coexist in photocatalysts. For example, the pump-and-probe spectroscopy by the femto-second laser for  $\text{TiO}_2$  nanocrystals suggested that defect sites affect the electron-hole pair recombination process, which depress the photocatalytic reaction by extinguishing 90% of the excited electrons.<sup>2)</sup> On the other hand, X. Chen *et al.* showed that a reduction of  $\text{TiO}_2$  nanocrystals enhances solar-driven photocatalytic activities.<sup>3)</sup> These results suggest that defects with different properties coexist in the  $\text{TiO}_2$  nanocrystal catalysts. The best way to clarify photocatalytic properties is to identify each defect site and track the electronic properties during photocatalysis.

Our recent zero field  $\mu$ SR measurements of a reduced rutile  $\text{TiO}_2$  single crystal at RIKEN-RAL showed atomic structure around the defect sites. The  $\mu$ -H complex in oxygen vacancy was observed, which corresponds to two hydrogens stabilized at the oxygen vacancy. The origin of hydrogen is not clear yet. The purpose of the present work is to clarify the origin of hydrogen by comparing two types of rutile  $\text{TiO}_2$ , prepared by Vernoulli method ( $\text{TiO}_2$ -H) and Floating Zone method ( $\text{TiO}_2$ -noH). It is known that  $\text{TiO}_2$ -H includes hydrogen as impurity while  $\text{TiO}_2$ -noH does not.

The  $\mu$ SR measurements were performed at the RIKEN-RAL Muon Facility. Mirror-polished rutile  $\text{TiO}_2$  single crystals ( $25 \times 25 \times 0.5 \text{ mm}^3$ , Crystal Base) oriented to the (110) plane were used. The oxygen vacancy was generated by performing reduction at 1173 K for 2 hr under an ultra-high vacuum ( $0.5 \times 10^{-8} \text{ Pa}$ ). The sample was irradiated with flash lamp light from the opposite side of the muon through a quartz glass

by utilizing the sample cell developed by Prof. Torikai's group.

The ZF  $\mu$ SR spectra before and after reduction were obtained for  $\text{TiO}_2$ -H and  $\text{TiO}_2$ -noH, respectively, at various temperatures from 4 K to room temperature. The muon stabilized site for the  $\text{TiO}_2$  without oxygen vacancy, whose spectra are shown in Fig. 1(a), has been reported by Shimomura *et al.*<sup>4)</sup> The site is next to the lattice oxygen with which the muon bonds. Characteristic oscillations for both the spectra suggest the existence of an isotropic magnetic field. The frequency was 0.8 MHz, corresponding to 5.9 mT at the muon site. The possible origin for the isotropic magnetic field is  $\text{Ti}^{3+}$ , which exists at the second neighbor site of the muon.<sup>4)</sup> Clear differences were observed after the reduction, which generated oxygen vacancies as shown in Fig. 1(b). The oscillation in the  $\text{TiO}_2$ -H spectra is attributed to the interaction with hydrogen in the oxygen vacancy, similar to what same as we previously found. The small Lorentzian type relaxation observed for  $\text{TiO}_2$ -noH could be explained by the magnetic interaction with nuclear spins of Ti ( $^{47}\text{Ti}$  and  $^{49}\text{Ti}$ ) ( $<0.2 \text{ mT}$ ), which suggests that no  $\mu$ -H interaction exists. The present study strongly supports the existence of  $\mu$ -H complex in oxygen vacancy by interacting with the existing H in  $\text{TiO}_2$ -H.

In addition, the photocatalytic properties of  $\mu$ -H complex were examined by pump-and-probe measurements. The details are still under analysis.

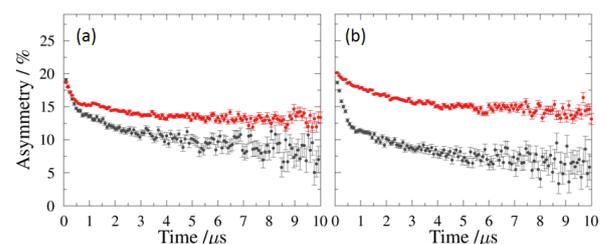


Fig. 1. Zero field  $\mu$ SR spectrum of rutile  $\text{TiO}_2$  (a) before and (b) after reduction. Black and red dots correspond to  $\text{TiO}_2$ -H (6 K) and  $\text{TiO}_2$ -noH (5 K).

## References

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