

Behavior of Oxygen During Photocatalytic CO₂ Conversion into Fuels Using Pd/TiO₂Hongwei Zhang¹ and Yasuo Izumi^{1,*}¹ Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan**1 Introduction**

Photocatalytic conversion of CO₂ into fuels is one of the routes to producing carbon neutral fuels without a net increase in atmospheric CO₂ concentrations associated with fossil-derived alternatives [1]. Pd nanoparticles supported on TiO₂ (Pd/TiO₂) were efficient for photocatalytic conversion of CO₂ [2], however, the photo-oxidation mechanism over the Pd/TiO₂ photocatalyst is still unclear. To clarify the mechanism of the photo-oxidation of water molecules, in situ Ti K-edge XAFS study was performed.

2 Experimental Section

Ti K-edge XAFS spectra were measured in the KEK Photon Factory on beamline 9A, 9C, and 12C. Pd K-edge XAFS results measured on beamline NW10A were already reported [3]. The storage ring energy was 2.5 eV and the ring current was 449.3–324.4 mA. A Si (1 1 1) double-crystal monochromator and a pair of bent conical/cylindrical mirrors and/or double flat mirrors were inserted into the X-ray beam path. Spectra for the Pd/TiO₂ sample (10 mg) diluted by boron nitride were measured in the presence/absence of UV–visible irradiation provided by a 500-W xenon arc lamp (Ushio) at the beamline. The Ti K-edge absorption energy was calibrated to 4964.5 eV using the spectrum of the 5- μ m-thick Ti foil. XAFS data were analyzed using the XDAP software package.

3 Results and Discussion

Under CO₂ (100 kPa), moisture (2.2 kPa), and UV–visible light, the change in coordination number $N(\text{Ti}-\text{O})$ was monitored for Pd/TiO₂ sample (Fig. 1A, C). In comparison to the initial value (6.0) under CO₂, moisture, and dark, the value significantly decreased to 4.9–5.7 (mean value 5.3) during light irradiation for 3.5 h. At 30 minutes after the light was off, the $N(\text{Ti}-\text{O})$ value increased to the original value (6.0). $N(\text{Ti}-\text{O}-\text{Ti})$ values followed a similar trend: decrease from initial 11.3 to 9.7–10.6 during the irradiation of UV–visible light and increase to 10.9 at 30 minutes after the light was off (Fig. 1B). Taking the experimental and fit errors into account (Fig. 1A, B), the $N(\text{Ti}-\text{O})$ and $N(\text{Ti}-\text{O}-\text{Ti})$ values would evaluate the concentration of oxygen vacancy (O_v) sites in/on TiO₂ semi-quantitatively.

Corresponding to the time course of Ti K-edge EXAFS, that of Ti K pre-edge region was also plotted (Fig. 1D–F). In comparison to data for fresh sample under CO₂ (100 kPa), moisture (2.2 kPa), and dark (Fig. 1D: 0 min), the peak pattern changed after the UV–visible light was irradiated, especially in the region between 4968 and

4971 eV (Fig. 1D: 5, 30 min). This trend is in good agreement with the increase of pre-edge peak at 4967.6 eV owing to 5 coordination Ti sites [4,5] or 4 coordination Ti sites [5] in comparison to that at 4968.8 eV owing to 6 coordination Ti sites [4]. Please note that there is minor energy calibration difference between reference 4 and this study.

While the peak pattern negligibly changed during the UV–visible irradiation (Fig. 1E: 60, 100, 130, 150 min; Fig. 1F: 180 min), the pattern clearly changed after the light was off (Fig. 1F: light off 0, 30 min). The last two peak patterns were very similar to that of fresh sample before light irradiation (Fig. 1D: 0 min), in consistent with the reversible change of the $N(\text{Ti}-\text{O})$ and $N(\text{Ti}-\text{O}-\text{Ti})$ values based on EXAFS analyses (Fig. 1A, B).

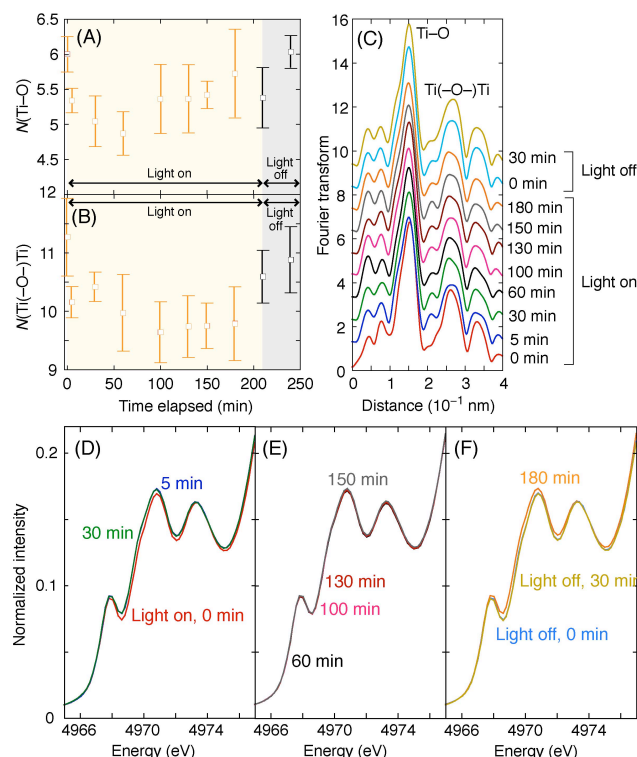
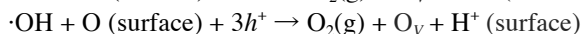
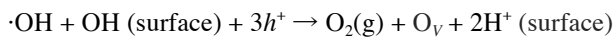


Fig. 1: Time course of Ti K-edge (A–C) EXAFS and (D–F) pre-edge region for Pd/TiO₂ photocatalyst (10 mg) under CO₂ (100 kPa) and moisture (2.2 kPa) for 3.5 h irradiated by UV–visible light and subsequently for 0.5 h under dark. The changes of (A) $N(\text{Ti}-\text{O})$ values, (B) $N(\text{Ti}-\text{O}-\text{Ti})$ values, and (C) Fourier transform of k^3 -weighted EXAFS χ function.

We consider the oxidation reaction using moisture on TiO₂ combined with Pd nanoparticles. Water is activated by a hole to form the ·OH radical



The subsequent reaction of ·OH with a surface hydroxy group/O atom is fast, e.g., to form O₂, an O_V site, and a proton(s) due to the nature of the radical reaction.



In fact, the concentration of O_V sites dramatically increases on/in TiO₂ as monitored by the decrease of the *N*(Ti–O) value from 6.0 for fresh sample to 4.9–5.7 and the *N*(Ti(–O–)Ti) value from 11.3 for fresh sample to 9.7–10.6 by the monitoring during the irradiation of UV–visible light (3.5 h) and darkness (0.5 h) (Fig. 1). The protons formed near the interface between the metal nanoparticle and the TiO₂ surface are transferred to the metal nanoparticle to form C-containing products or H₂, whether they encounter CO₂-derived species and hot/excited electrons, or such electrons only [6]. Effectively separated redox sites are nicely conjugated to transport protons between them, similar to photosystems.

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